

HYDROGEOCHEMICAL EXPLORATION AT TSUMEB

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VOLUME 1B: PLATES AND APPENDICES

The University of Cape Town

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PLATE 1. A typical windpump near Tsumeb. Note the characteristic acacia vegetation, the ubiquitous fragments of calcrete and the dolomitic hills of the Otavi Mountainland in the background. →→→

PLATE 2. A borehole installation near Tsumeb. The pump is driven by a belt connected to a diesel engine. →→→






PLATE 3. A borehole in the Tsumeb mine. The dip of the hole is nearly flat. >>>>

PLATE 4. Water running from an old orebox in the upper levels of the Tsumeb mine. >>>>



PLATE 5. Water spraying from a fissure in the roof of a drive in the upper levels of the Tsumeb mine. The rock is fractured dolomite. Note the sampling tag. →→→→

PLATE 6. Growths of hard, green carbonate on the walls and floor of a drive in the upper levels of the Tsumeb mine. →→→→



APPENDIX A

*Orientation survey of Tsumeb mine water:
Technical data for the 36 sampling points*

CONTENTS

page

Abbreviations used

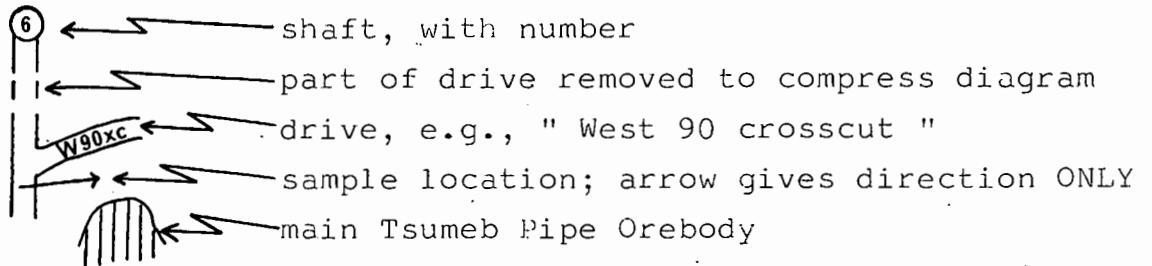
A1

Technical data

A2-A37

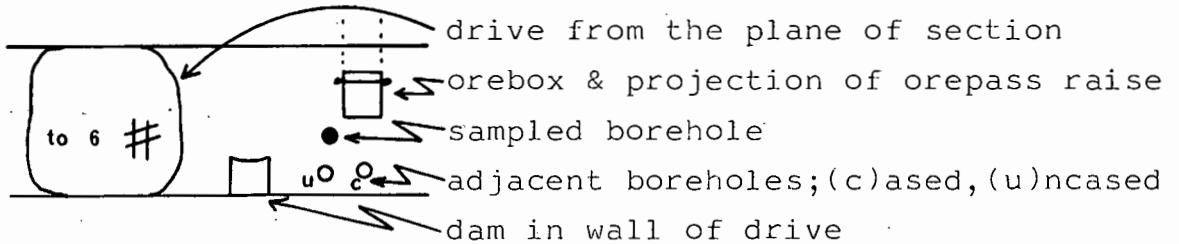
ABBREVIATIONS AND SYMBOLS FOR APPENDIX A
 TSUMEB MINE WATER ORIENTATION SURVEY:
 Technical Data for the 36 sampling points.

ABBREVIATIONS: (N)orth, (S)outh, (E)ast, (W)est, (H)aulage, (Max)imum, (M)inimum, XC= crosscut, - = irrelevant or untraceable. Numbers in () are estimates. 6# = shaft with N^o.
SYMBOLS USED IN PLAN SKETCHES (not to scale).



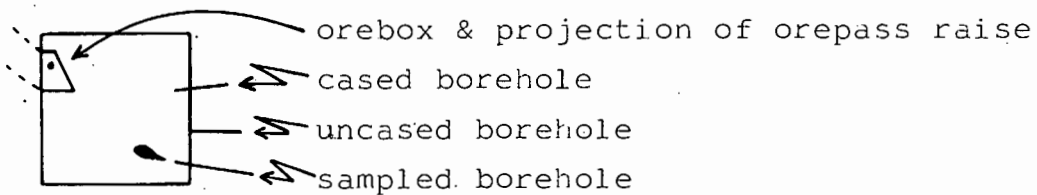
SYMBOLS USED IN LONG SECTION SKETCHES (not to scale).

(N.B. Standard drive is 2,4m high, mean).



SYMBOLS USED IN CROSS SECTION SKETCHES (not to scale).

(N.B. Standard drive is 2,4m high by 3,2m wide, mean).



GENERAL SYMBOLS (self-explanatory symbols not shown here).

- size of man gives scale in non-standard Sections
- sample point or flow path
- galvanised pipe with tap
- wall
- fractures
- pipe, not borehole
- pool of water
- rubber hose

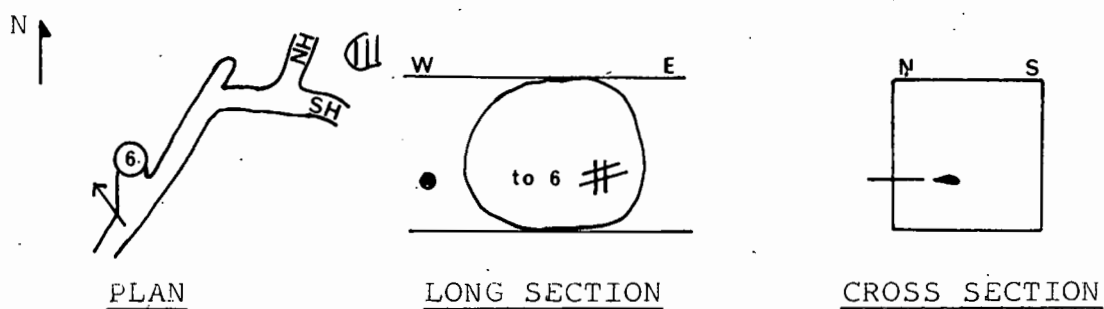
APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:
 Technical Data for the 36 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

Sample N^o.: 131 Mine Level: 34
Co-ordinates: 1797 E 1837 N Date Sampled: 5 June 1973
Location: In the north wall of the north haulage, about
 5m west of six shaft.

Description: A single, flat borehole. Drinking water
 hole.



TCL Borehole N^o.: - Type: -
Length: - Dip: (Flat) Azimuth: (280^o)
Core Size: (4cm) Date of Origin: Min. 10 years old.
Purpose: Probably drilled to obtain drinking water.

Water intersected at: - Yield: -

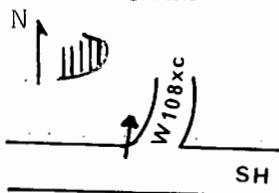
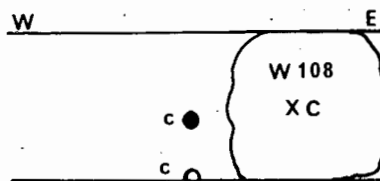
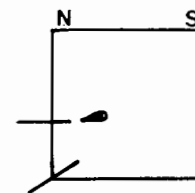
Geology Etc.: No traceable log. Drilled away from the ore
 body. Well to the west of any known ore.

APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:

Technical Data for the 36 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

Sample N^o: 132Mine Level: 34Co-ordinates: 1868 E 1826 N Date Sampled: 5 June 1973Location: In the north wall of the south haulage, on the west corner of W 108 XC. One metre from the floor.Description: Upper of two cased holes in a vertical row, the lower one near the join between floor & wall. Casing corroded right back into the dolomite.PLANLONG SECTIONCROSS SECTIONTCL Borehole N^o: 2735Type: Diamond drillLength: 71,6m Dip: FlatAzimuth: 024^oCore Size: Ax (49,2 mm) Date of Origin: Nov 1967Purpose: To test the ore.Water intersected at: 36,6m Yield: 0,5 l/secGeology Etc.: Grey dolomite, in places calcitised.

Pseudo-aplite from 32,9-34,4 m. Moderate mineralisation from 30,5 to 67,1 m (4,2% Cu, 1,7% Pb and 0,7% Zn). The ore was pristine at the time of sampling.

APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:

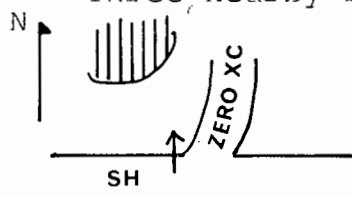
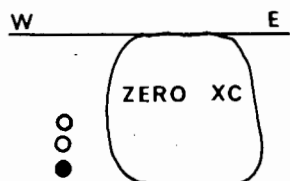
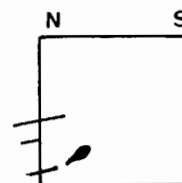
Technical Data for the 35 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

Sample N^o: 133 Mine Level: 34
Co-ordinates: 1971 E 1798 N Date Sampled: 5 June 1973
Location: In the north wall of the south haulage, on
the western corner of Zero crosscut.

Description:* Lowermost of three holes in a row. Two,
cased, middle one uncased and shallow.

Three nearby bolts. Casings large & thick. Artesian.

PLANLONG SECTIONCROSS SECTION

TCL Borehole N^o: 2806 Type: Diamond drill
Length: 61,0m Dip: -35° Azimuth: 024°
Core Size: AX(49,2 mm) Date of Origin: Nov. 1968
Purpose: To test the ore.

Water intersected at: - Yield: -

Geology Etc.: Siliceous dolomite, massive calcite, cavities.
Good disseminated mineralisation from 27,4-
56,4m (10% Cu, 10% Pb & 6% Zn). Massive ore from 44,5-
46,6m (10% Cu, 37% Pb & 5% Zn). The ore was pristine
at the time of sampling.

* Dried up by May 1975.

APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:
 Technical Data for the 36 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

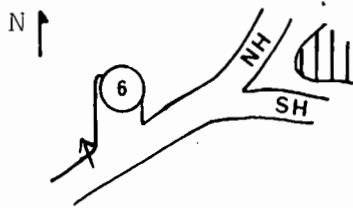
Sample N^o: 134

Mine Level: 35

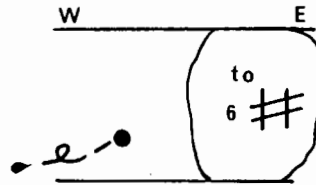
Co-ordinates: 1797 E 1837 N Date Sampled: 5 June 1973

Location: In the north wall of the north haulage, just west of 6 shaft. About one metre from the floor.

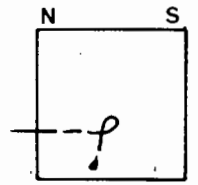
Description: A single, flat hole with a rubber hose attached, drinking water hole.



PLAN



LONG SECTION



CROSS SECTION

TCL Borehole N^o: -

Type: -

Length: -

Dip: (Flat)

Azimuth: (280°)

Core Size: (4 cm)

Date of Origin: About 1965

Purpose: Probably drilled for drinking water.

Water intersected at: -

Yield: -

Geology Etc.:

No traceable log. Drilled in dolomite, away from the orebody. Not near any known ore.

APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:

Technical Data for the 35 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

Sample N^o: 135

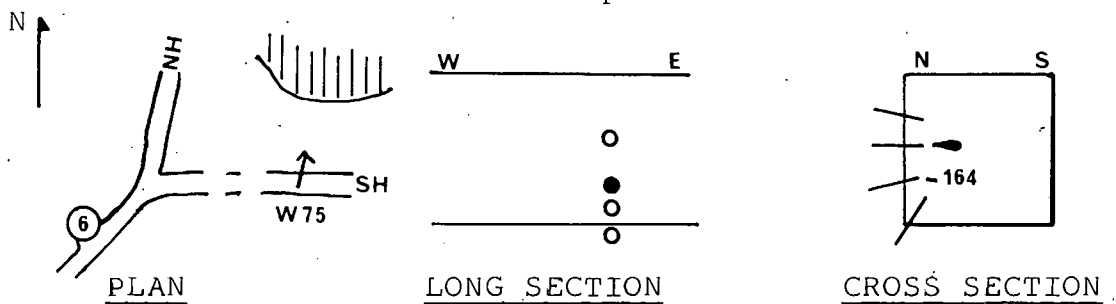
Mine Level: 35

Co-ordinates: 1916E 1821N

Date Sampled: 5 June 1973

Location: In the north wall of the south haulage, at about W 75 section. Within one metre of sample point 164.

Description: One of a vertical row of four boreholes, the lowest of which is in the floor. 135 is the 2nd from the top.



TCL Borehole N^o: 2759

Type: Diamond drill

Length: 51,8 m

Dip: Flat

Azimuth: 024^o

Core Size: AX (49,2 mm)

Date of Origin: Sept. 1968

Purpose: To test the ore.

Water intersected at: 28,7

Yield: 0,5 litres/second

Geology Etc.: Drilled in siliceous dolomite. Moderate mineralisation (mainly Cu oxide/sulphide from 13,7 to 35,0 m. Massive ore intersection from 29,0 to 29,9 m (cerusite- galena).

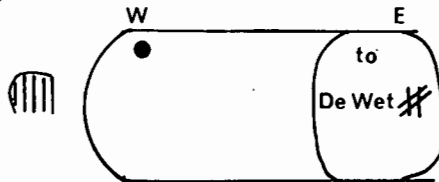
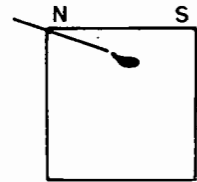
The ore was pristine at the time of sampling.

APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:

Technical Data for the 36 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

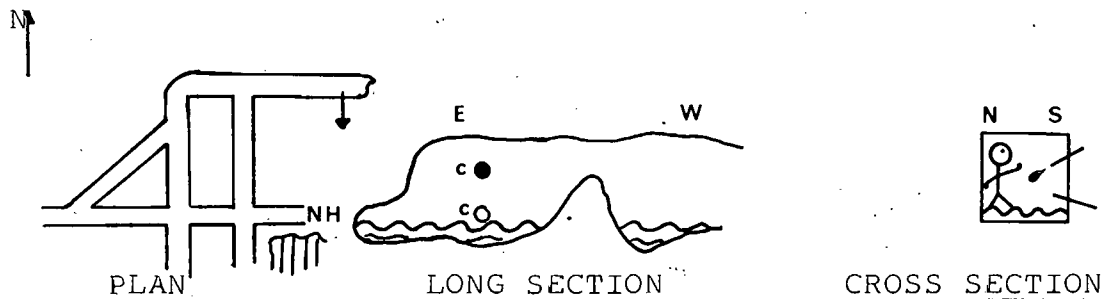
Sample N^o: 136Mine Level: 37Co-ordinates: 1686 E 1771 N Date Sampled: 5 June 1973Location: High in the north wall at the end of a short
drive just west of De Wet Shaft.Description: A single, cased hole.PLANLONG SECTIONCROSS SECTIONTCL Borehole N^o: -Type: -Length: - Dip: +(40°) Azimuth: (280°)Core Size: (4cm)Date of Origin: Min. 10 years oldPurpose: Probably a drinking water or cementation hole.Water intersected at: -Yield: -Geology Etc.: No traceable log. Dolomite area. Drilled
away from the ore, well west of the ore
body.

APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:

Technical Data for the 35 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

Sample N^o: 137Mine Level: 27Co-ordinates: 2016 E 1863 N Date Sampled: 8 June 1973Location: Three metres from the northern end of the long drilling drive to the north from the north haulage. About 1m from the floor.Description: Borehole with a large rotary stopcock. Upper of two cased boreholes in line.TCL Borehole N^o: 2424Type: Diamond drillLength: 30,5m Dip: + 32^oAzimuth: 204^oCore Size: AX (49,2 mm) Date of Origin: 1964Purpose: Drilled to test the North Break orebody.Water intersected at: - Yield: -

Geology Etc.: Altered ferruginous and calcitised dolomite. Mineralised between 1,8m - 7,6m (1,5 % Cu, 5 % Pb & 1 % Zn). The ore was pristine at the time of sampling.

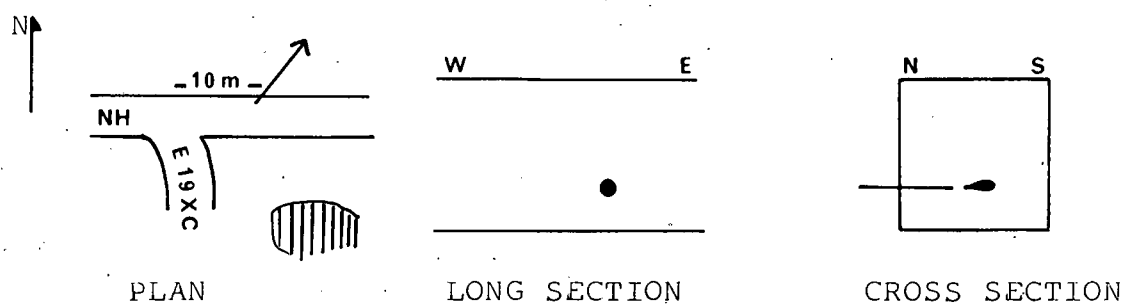
APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:
 Technical Data for the 36 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

Sample N^o: 138 Mine Level: 28
Co-ordinates: 2020 E 1816 N Date Sampled: 8 June 1973
Location: In the north wall of the north haulage, about
 10 m east of E 19 crosscut.

Description: A single, flat, cased hole.



TCL Borehole N^o: 2815 Type: Diamond drill
Length: 67 m Dip: Flat Azimuth: 024^o
Core Size: AX(49,2 mm) Date of Origin: Dec. 1968
Purpose: Probably water cover.

Water intersected at: 51 m Yield: 0,21 l/sec.

Geology Etc.: Drilled in dolomite. Only very slight
 mineralisation (malachite, arsenates).

APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:

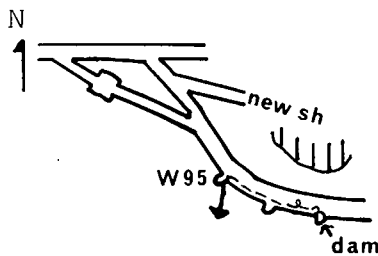
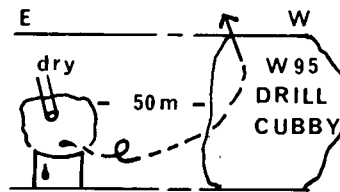
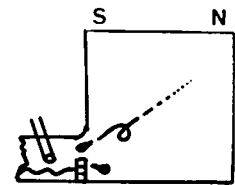
Technical Data for the 36 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

Sample N^o: 139Mine Level: 30Co-ordinates: *1870 E 1768 NDate Sampled: 8 June 1973

Location: A dam set in the south wall of the south haulage, fed by a borehole in the roof of W 95 diamond drill cubby, via a 50m length of rubber hose.

Description: Concrete dam** fed only from W 95 hole, via the hose.

PLANLONG SECTIONCROSS SECTIONTCL Borehole N^o: H 1882Type: Diamond drillLength: 47,2 mDip: + 35°Azimuth: 204°Core Size: EX(38,1 mm)Date of Origin: * 1957

Purpose: Hole drilled to test the S 95 manta orebodies south of the main pipe.

<u>Water intersected at:</u>	34,4m	<u>Yield:</u>	5,6 l/sec
	36,9m		11,3 " (cemented)
<u>Geology Etc.:</u>	39,6m		4,2 "
	44,5m		4,2 "
	46,6m		5,3 "
	47,2m		7,4 "

⊙ Dolomite with chert, slightly altered (Mn). Ore between 29,6 - 30,0m (21,7% Cu, 0,2% Pb & 0,7% Zn). Ore was pristine at the time of sampling.

*= Refers to borehole. Dam co-ordinates 1903 E 1733 N.

Dam is a waste water holding dam fed by borehole H 1882.

**= Dam annihilated subsequently by opening of S 110 Drive West.

APPENDIX ATSUMEB MINE WATER ORIENTATION SURVEY:

Technical Data for the 36 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

Sample N^o: 140

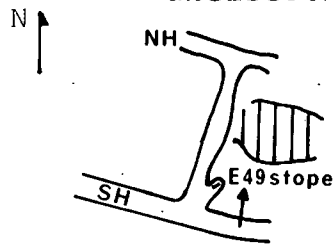
Mine Level: 28

Co-ordinates: 2090 E 1695 N Date Sampled: 8 June 1973

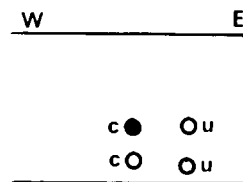
Location: In the north wall of the south haulage, 13m east of E 49 stope entrance (= E 65 XC).

Hole is 1½ m from the floor.

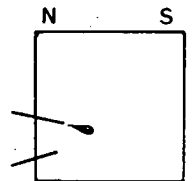
Description: Upper left of four holes in a square pattern, left two cased, right two uncased. Old casings.



PLAN



LONG SECTION



CROSS SECTION

TCL Borehole N^o: 2877

Type: Diamond drill

Length: 30m

Dip: + 10°

Azimuth: 024°

Core Size: AX (49,2 mm)

Date of Origin: 1971

Purpose: Drilled to test the ore.

Water intersected at: -

Yield: -

Geology Etc.: Drilled in dolomite. Intersected massive ore (oxide/sulphide; up to 41,4% Cu, 19,0% Pb & 0,8% Zn), from 10 -17m. The ore was pristine at the time of sampling.

APPENDIX A

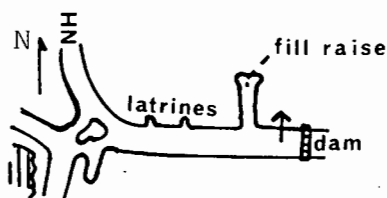
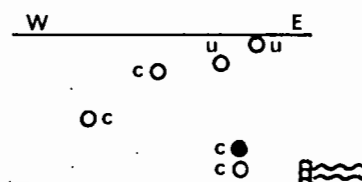
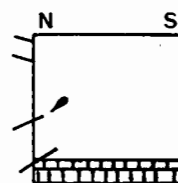
TSUMEB MINE WATER ORIENTATION SURVEY:

Technical Data for the 36 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

Sample N^o: 141 Mine Level: 27
Co-ordinates: 2077 E 1750 N Date Sampled: 8 June 1973
Location: In the far northeast corner of the orebody.

In the north wall, about 6m east of crosscut to main fill raise & 15m east of two latrines. Just west of dam.
Description: Second lowest of a dispersed group of 5 holes. Cased. About 30 cm from the floor. Artesian.

PLANLONG SECTIONCROSS SECTION

TCL Borehole N^o: - Type: Probably percussion.
Length: (Max 60m) Dip: - (20°) Azimuth: (010°)
Core Size: (4 cm) Date of Origin: About 15 years old.
Purpose: Probably cementation or drainage holes for the fill raise area.

Water intersected at: - Yield: -

Geology Etc.: No traceable log. Drilled in dolomite, away from the orebody. Well to the northeast of any known ore.

APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:
 Technical Data for the 36 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

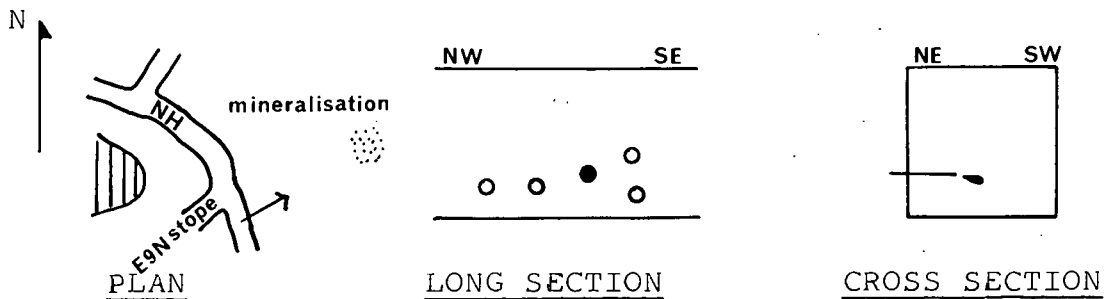
Sample N^o: 142

Mine Level: 30

Co-ordinates: 2050 E 1817 N Date Sampled: 8 June 1973

Location: In the north wall of the north haulage, just
 east of east 9 north stope.

Description: Central hole of a group of 5 holes, all
 approximately flat.



TCL Borehole N^o: 2864

Type: Diamond drill

Length: 287 m Dip: -5°

Azimuth: 052°

Core Size: AX (49,2 mm) Date of Origin: Nov. 1970

Purpose: To investigate the mineralised zone in the
 footwall of the orebody.

Water intersected at: 265 m Yield: 42 litres/ sec*

Geology Etc.: Dolomite mainly. Some Zn-Pb mineralisation
 from 133,5 to 135,3 m, from 144,5 to 145,0 m
 and especially between 202,7 and 207,3 m. The ore was
 pristine at the time of sampling.

* The hole may have been plugged, since 1973 flow rate was
 only about 4 l/second.

APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:
 Technical Data for the 36 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

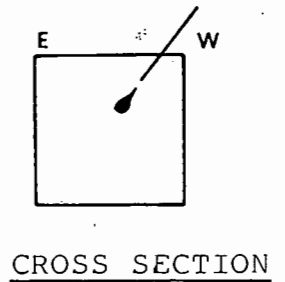
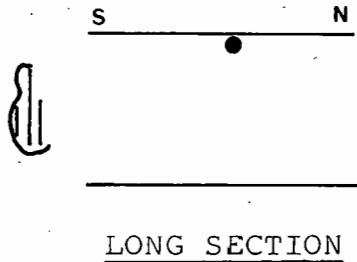
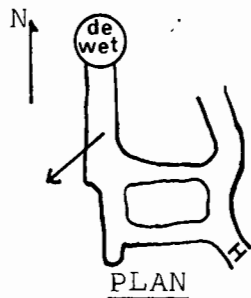
Sample N^o: 143

Mine Level: 22

Co-ordinates: 1700 E 1786 N Date Sampled: 8 June 1973

Location: About 10 m from De Wet Shaft

Description: A single cased hole near the junction of the wall and the roof, on the west side.



TCL Borehole N^o: -

Type: Probably percussion

Length: (Max 60 m) Dip: +(45°)

Azimuth: (235°)

Core Size: (4cm)

Date of Origin: About 1953

Purpose: Probably cementation cover for De Wet Shaft.

Water intersected at: -

Yield: -

Geology Etc.: No traceable log. Drilled away from the orebody. Far west of the ore.

APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:
 Technical Data for the 36 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

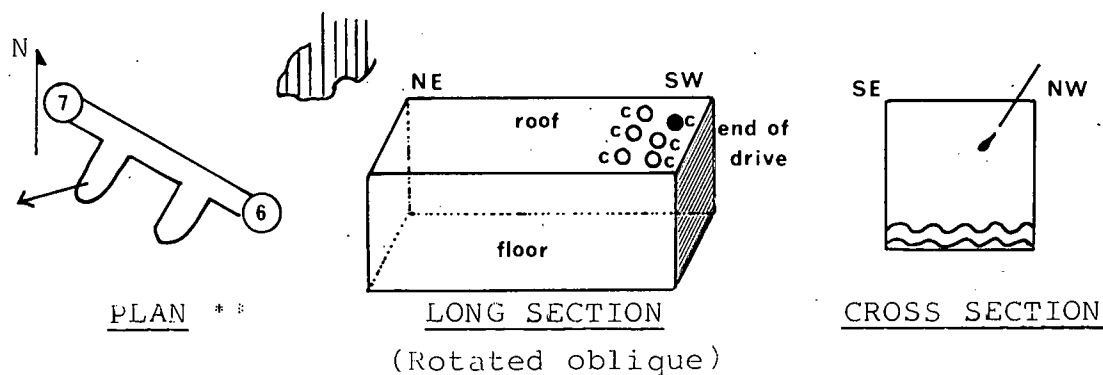
Sample N^o: 144

Mine Level: 42

Co-ordinates: 1764 E 1860 N Date Sampled: 13 June 1973

Location:* In the western side of the roof of a short southerly drive to an ore pass raise, the first such drive off the main drive from 7 shaft.

Description: One of six adjacent cased boreholes, all in the roof.



TCL Borehole N^o: - Type: Percussion

Length: Max 60m Dip: +(80°) Azimuth: (200°)

Core Size: (4 cm) Date of Origin: 1970-1

Purpose: Unknown. Possibly cementation cover for the raise.

Water intersected at: - Yield: -

Geology Etc.: No traceable log. Dolomite only. Far from any ore, drilled away from the orebody.

* Sampling site now destroyed by raise (1975).

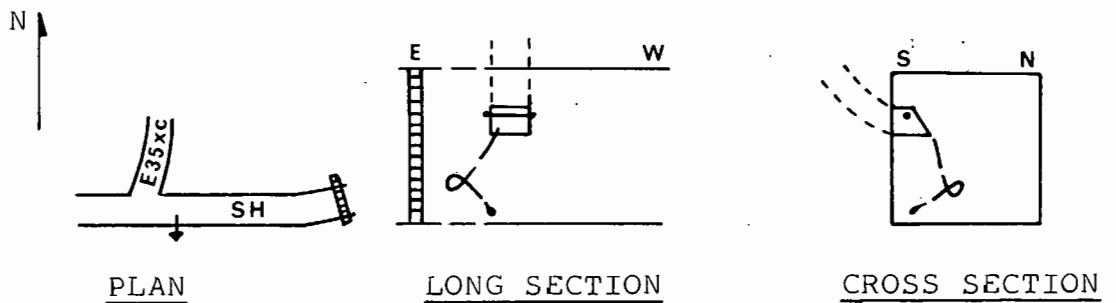
** There was less development in 1973 than is shown here.

APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:
 Technical Data for the 35 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

Sample N^o: 145 Mine Level: 24
Co-ordinates: 1968 E 1658 N Date Sampled: 12 June 1973
Location: On the south wall of the south haulage, just
 east of E 35 crosscut. Some 26m from the wall
 which now (1975) blocks the haulage at the eastern end.
Description: An orebox, drained by about 1m of rubber
 hose.



TCL Borehole N^o: - Type: -
Length: - Dip: - Azimuth: -
Core Size: - Date of Origin: About 1968
Purpose: Orebox regulates flow of broken ore from
 ore pass raise to ore train. Dormant.

Water intersected at: - Yield: -

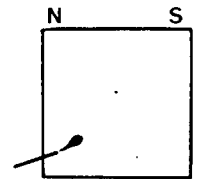
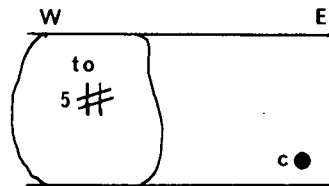
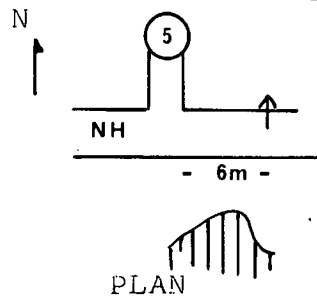
Geology Etc.: Somewhat south of the orebody. Water
 comes from stopes above 24 level, filled
 with waste.

APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:

Technical Data for the 36 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

Sample N^o: 146Mine Level: 26Co-ordinates: 1988 E 1791 N Date Sampled: 12 June 1973Location: In the north wall of the north haulage, 6m east of 5 shaft. About 30 cm from the floor.Description: A single artesian borehole between two iron bolts. The casing is old and corroded.TCL Borehole N^o: 2209Type: Diamond drillLength: 91,4 m Dip: -31°Azimuth: 024°Core Size: EX(38,1 mm)Date of Origin: 1959Purpose: Drilled to test ore possibly related to the North Break Ore, north of the main orebody.Water intersected at: 77,4-79,9m Yield: 2,8 l/sec
83,8 4,7 l/sec*Geology Etc.: Mainly dolomite with chert bands.

Mineralisation as follows:

59,4 - 61,0m : 3,1% Cu, 1,1% Pb & 0,7% Zn

76,2 - 77,7m : 0,6% Cu, 1,4% Pb & 1,32% Zn

83,5 - 84,1m : 3 % Cu, 20% Pb & 2% Zn. The ore was pristine at the time of sampling.

* Dropped considerably by 1975

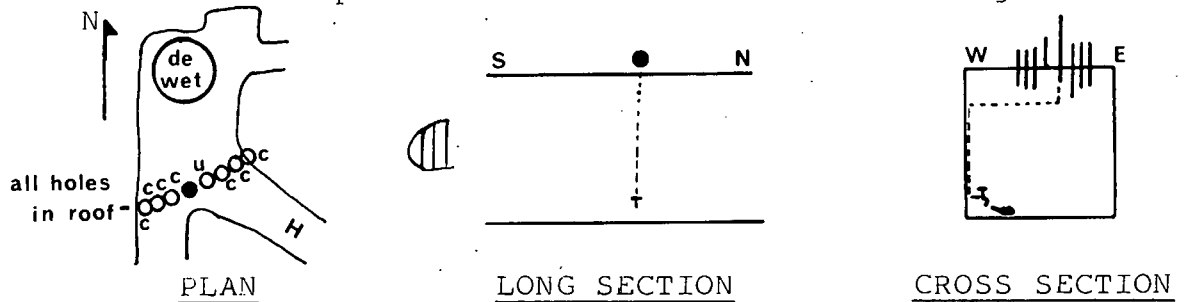
APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:
 Technical Data for the 36 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

Sample N^o: 147 Mine Level: 24
Co-ordinates: 1700 E 1784 N Date Sampled: 12 June 1973
Location: In the roof, a few metres south of De Wet Shaft.

Description: Borehole in the roof, with about 8m of galvanised pipe leading to a drinking water tap. Borehole is one of a row of eight.



TCL Borehole N^o: - Type: Probably percussion
Length: (Max 60m) Dip: (90^o) Azimuth: Indeterminate
Core Size: (4 cm) Date of Origin: About 1953
Purpose: Probably cementation cover for De Wet Shaft.

Water intersected at: - Yield: -

Geology Etc.: No traceable log. Dolomite only. Far west of any ore. Drilled nearly vertically.

APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:
 Technical Data for the 36 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

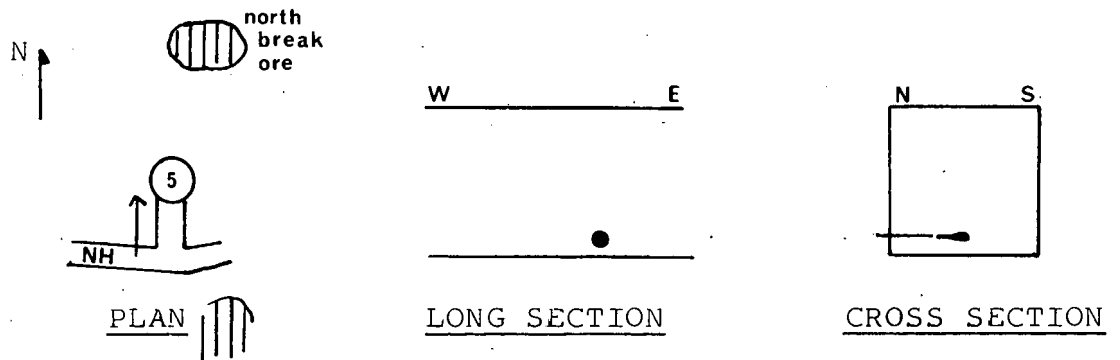
Sample N^o: 148

Mine Level: 26

Co-ordinates: 1968 E 1796 N Date Sampled: 12 June 1973

Location: In the north wall of the north haulage, about
 15 m west of 5' shaft.

Description: A single, flattish hole.



TCL Borehole N^o: 2947

Type: Diamond drill

Length: 97,5 m Dip: + 16°

Azimuth: 024°

Core Size: -

Date of Origin: May 1973

Purpose: To delineate the North Break Orebody.

Water intersected at: - Yield: -

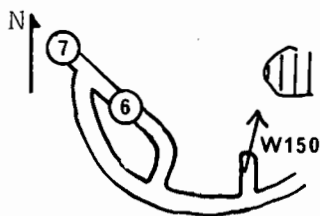
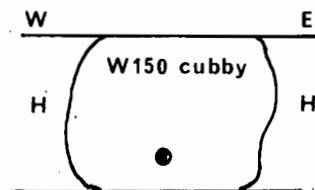
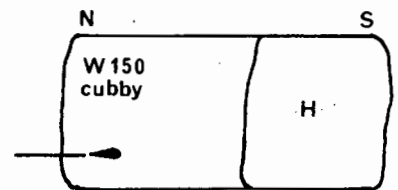
Geology Etc.: Drilled above the main North Break ore lode. Generally fractured, Zone 6 dolomite throughout. Narrow intersection of slight grade vanadates and arsenates at 78 m. The ore was pristine at the time of sampling.

APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:

Technical Data for the 36 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

Sample N^o: 149Mine Level: 44Co-ordinates: 1825 E 1803N Date Sampled: 13 June 1973Location: At the end (i.e. 1973 end) of W150 diamond drill cubby. (Opposite sample number 153).Description: A single, flat, cased hole about one metre from the floor.PLANLONG SECTIONCROSS SECTIONTCL Borehole N^o: 2950Type: Diamond drillLength: 79,2 m Dip: FlatAzimuth: 024^oCore Size: -Date of Origin: May 1973Purpose: To explore the orebody.Water intersected at: -Yield: -

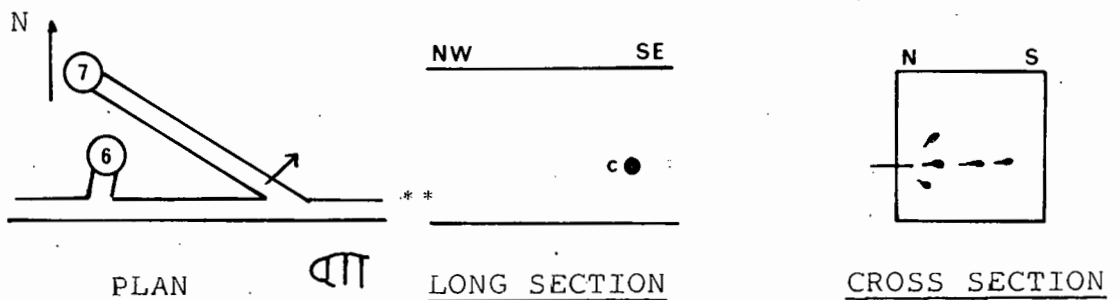
Geology Etc.: Zone 5 dolomites. Minor Cu, Pb, Zn ore from 42,4 to 43,3 m and from 54,3 to 55,2 m. The ore was pristine at the time of sampling.

APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:
 Technical Data for the 35 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

Sample N^o: 150 Mine Level: 38
Co-ordinates: 1827 E 1842 N Date Sampled: 13 June 1973
Location: In the north wall of the drive from 7 shaft
 to the north haulage, about 6m from the
 junction thereof. About one metre from the ground.
Description: A single cased borehole with a high pressure rotary stopcock.*



TCL Borehole N^o: - Type: Probably percussion.
Length: (Max 60m) Dip: +(5°) Azimuth: (30°)
Core Size: (4 cm) Date of Origin: About 1971
Purpose: Probably de-watering hole.

Water intersected at: - Yield: No record. Extreme.

Geology Etc.: No traceable log. Drilled in dolomite,
 away from the ore. Not near any known ore.

* Now plugged (1975).

** This drive has now been developed into the N. Haulage.

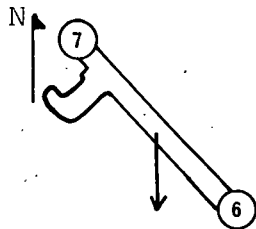
APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:
 Technical Data for the 36 sampling points.

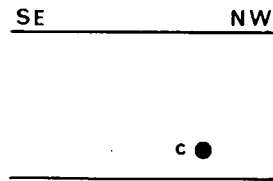
KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

Sample N^o: 151 Mine Level: 41
Co-ordinates: 1780 E 1868 N Date Sampled: 13 June 1973
Location: In the south wall, half way along the drive
 between 7 and 6 shafts.

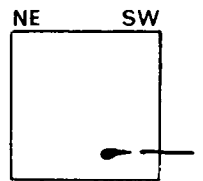
Description: A single, cased hole.



PLAN



LONG SECTION



CROSS SECTION

TCL Borehole N^o: - Type: Percussion
Length: Max 60m. Dip: (Flat) Azimuth: (180^o)
Core Size: (4 cm) Date of Origin: About 1970
Purpose: Unknown. Maybe mining development hole of
 some kind.

Water intersected at: - Yield: -

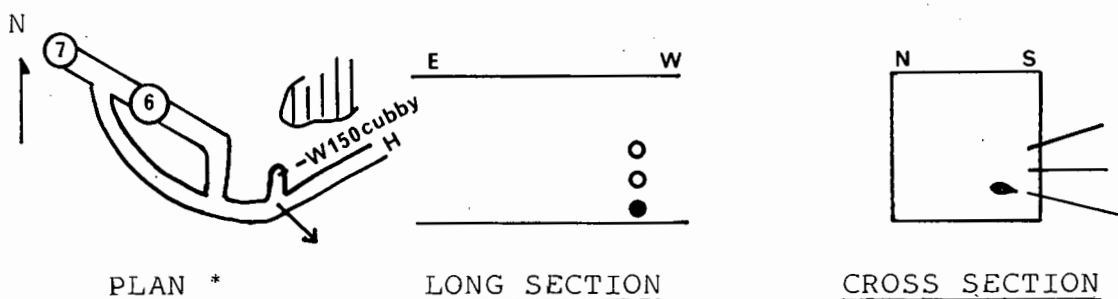
Geology Etc.: No traceable log. Country rock dolomite.
 No nearby ore. Drilled away from the
 main orebody.

APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:

Technical Data for the 36 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

Sample N^o: 153Mine Level: 44Co-ordinates: 1824 E 1793 N Date Sampled: 13 June 1973Location: Low in the south wall of the south haulage, opposite W 150 diamond drill cubby and thus opposite sample point number 149.Description: Lowermost of three adjacent holes, all cased. Artesian.TCL Borehole N^o: -Type: PercussionLength: Max 60m. Dip: $-(45^\circ)$ Azimuth: (160°) Core Size: (4 cm)Date of Origin: About 1972Purpose: Unknown. Possibly cementation cover for drive.Water intersected at: -Yield: -Geology Etc.: No traceable log. Dolomite area. Hole directed away from the main ore zones, but may have entered a region of weak mineralisation.

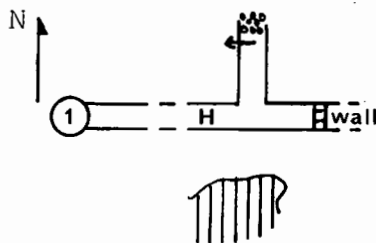
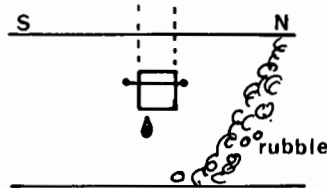
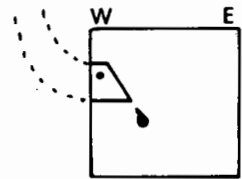
* Considerable development on this level since sampling.

APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:
 Technical Data for the 36 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

Sample N^o.: 154 Mine Level: 10
Co-ordinates: 1982 E 1986 N Date Sampled: 15 June 1973
Location: In the west wall, two metres from the present
 (1975) northeast end of the accessible part of
 the level.
Description: An old, open, wooden orebox, at the bottom
 of an old ore pass raise.

PLANLONG SECTIONCROSS SECTION

TCL Borehole N^o.: - Type: -
Length: - Dip: - Azimuth: -
Core Size: - Date of Origin: Min. 40 years old
Purpose: Passes ore from raise to ore train. Long dormant.

Water intersected at: - Yield: -

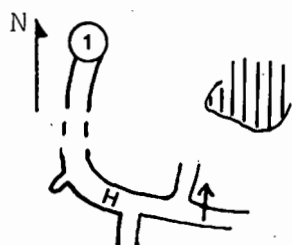
Geology Etc.: The box is north of the inclined orebody at
 this level, but below it. The water possibly
 comes from filled stopes on 8 and 9 levels, which contain
 waste. The stream cannot be definitely traced.

APPENDIX A

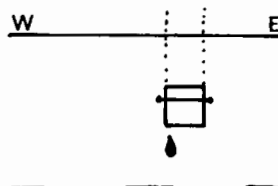
TSUMEB MINE WATER ORIENTATION SURVEY:
 Technical Data for the 36 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

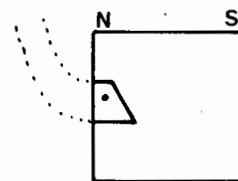
Sample N^o: 155 Mine Level: 16
Co-ordinates: 1954 E 1834 N Date Sampled: 15 June 1973
Location: The 1st orebox in the main drive between 1 & 3
 shafts, just past the short drive to the downcast
 vent raise. In the north wall of the drive.
Description: Orebox.



PLAN



LONG SECTION



CROSS SECTION

TCL Borehole N^o: - Type: -
Length: - Dip: - Azimuth: -
Core Size: - Date of Origin: About 1940
Purpose: Controls flow of broken ore from ore pass
 raise to ore train.

Water intersected at: - Yield: -

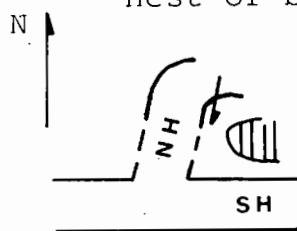
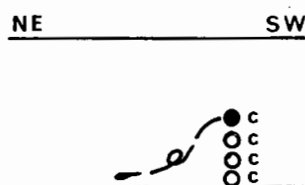
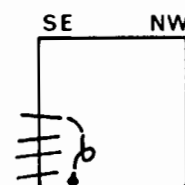
Geology Etc.: The water is draining through filled
 stopes on 14 & 15 levels. The fill is
 waste, of average low grade mineral content.

APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:

Technical Data for the 36 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

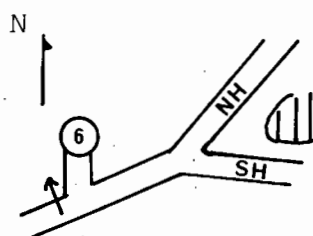
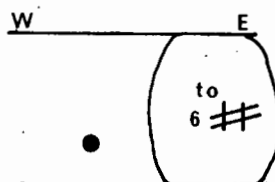
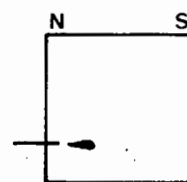
Sample N^o: 156Mine Level: 32Co-ordinates: 1856 E 1909 N Date Sampled: 14 June 1973Location: In the south wall of the north haulage,
about 5m into the turn where the haulage
curves around from S-N to W-E.Description: Uppermost of four holes in a vertical row,
all cased, oblique to the wall, amid a
nest of bolts. Has 3m of rubber hose attached.PLANLONG SECTIONCROSS SECTIONTCL Borehole N^o: 2843Type: Diamond drillLength: 67,4m Dip: + 10°Azimuth: 204°Core Size: AX (49,2 mm)Date of Origin: Mar 1969Purpose: To test the ore.Water intersected at: - Yield: -Geology Etc.: Drilled into the western end of the main
orebody. Country rock is silicified
dolomite. Poor sulphidic mineralisation as follows:
31,1-32,6m : 0,7% Cu, 2,6% Pb & 2,0% Zn.
38,7-39,6m : trace Cu, 2,5% Pb & 1,0% Zn. The ore
was pristine at the time of sampling.

APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:

Technical Data for the 36 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

Sample N^o.: 157Mine Level: 31Co-ordinates: 1797 E 1835 N Date Sampled: 14 June 1973Location: In the north wall of the north haulage,
just west of 6 shaft.Description: Single flat hole, drinking water.PLANLONG SECTIONCROSS SECTIONTCL Borehole N^o.: - Type: -Length: - Dip: (Flat) Azimuth: (285°)Core Size: (4 cm) Date of Origin: Min 10 years oldPurpose: Probably drilled for drinking water.Water intersected at: - Yield: -Geology Etc.: No traceable log. Hole drilled in dolomite,
away from the orebody. Not near any known
mineralisation.

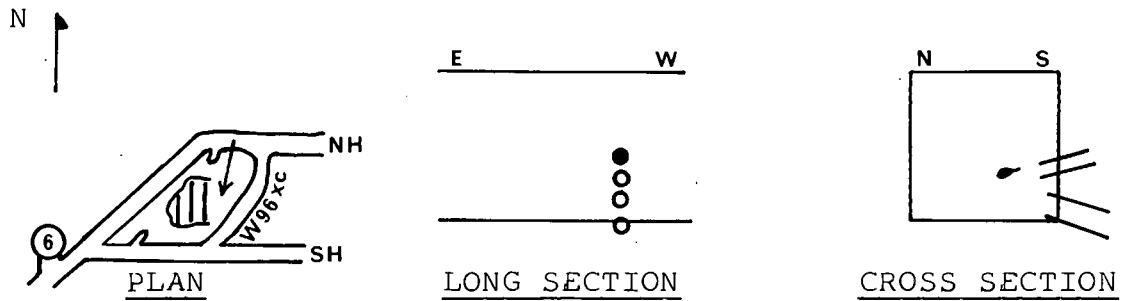
APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:
 Technical Data for the 36 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

Sample N^o: 158 Mine Level: 31
Co-ordinates: 1909 E 1881 N Date Sampled: 14 June 1973
Location: In the south wall of the north haulage, about
 15m west of W 96 crosscut.

Description: Uppermost of four inclined cased holes. The
 upper two inclined up, the lower two down.



TCL Borehole N^o: 2412 Type: Diamond drill
Length: 84m Dip: + 32° Azimuth: 204°
Core Size: (AX 49,2 mm) Date of Origin: Min 10 years old
Purpose: Exploration of the orebody.

Water intersected at: - Yield: -

Geology Etc.: Hole intersects ore and pseudo-aplite.
 Moderate Cu mineralisation (sulphide and
 some oxide) between 23 and 84m. Ore was pristine at the
 time of sampling.

APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:
 Technical Data for the 36 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

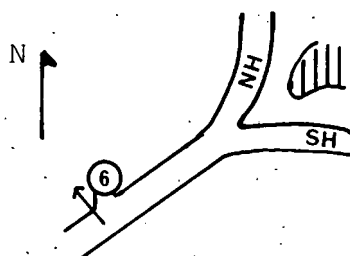
Sample N^o: 159

Mine Level: 32

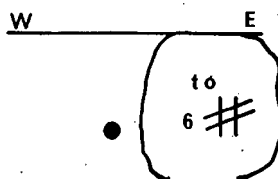
Co-ordinates: 1797 E 1837 N Date Sampled: 14 June 1973

Location: In the north wall of the north haulage, just west of 6 shaft.

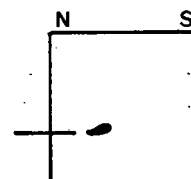
Description: A single borehole. Drinking water hole.



PLAN



LONG SECTION



CROSS SECTION

TCL Borehole N^o: -

Type: -

Length: - Dip: (Flat) Azimuth: (280°)

Core Size: (4 cm)

Date of Origin: Min 10 years old.

Purpose: Probably drilled for drinking water.

Water intersected at: -

Yield: -

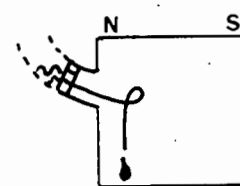
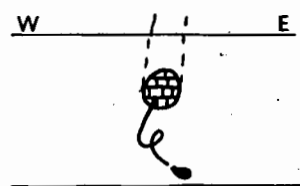
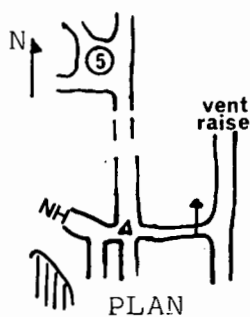
Geology Etc.: No traceable log. Drilled in dolomite, away from the orebody. Far to the west of any known ore.

APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:
 Technical Data for the 36 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

Sample N^o: 160 Mine Level: 20
Co-ordinates: 2015 E 1729 N Date Sampled: 15 June 1973
Location: In the north wall in the extreme north east
 corner of the north haulage, just before a
 short drive to the main vent raise.
Description: A 3 m long rubber hose draining a
 sealed ventilation or fill raise.



PLAN

LONG SECTION

CROSS SECTION

TCL Borehole N^o: - Type: -
Length: - Dip: - Azimuth: -
Core Size: - Date of Origin: About 1955
Purpose: Drainage of raise, which is now sealed and
 dormant.

Water intersected at: - Yield: -

Geology *Etc.: The water probably comes from between 19 &
 20 levels, not directly from the ore areas
 but quite nearby. The sample point is a bit north of and
 below the inclined orebody. Kersantite occurs 20 m to
 the west of the raise.

APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:

Technical Data for the 36 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

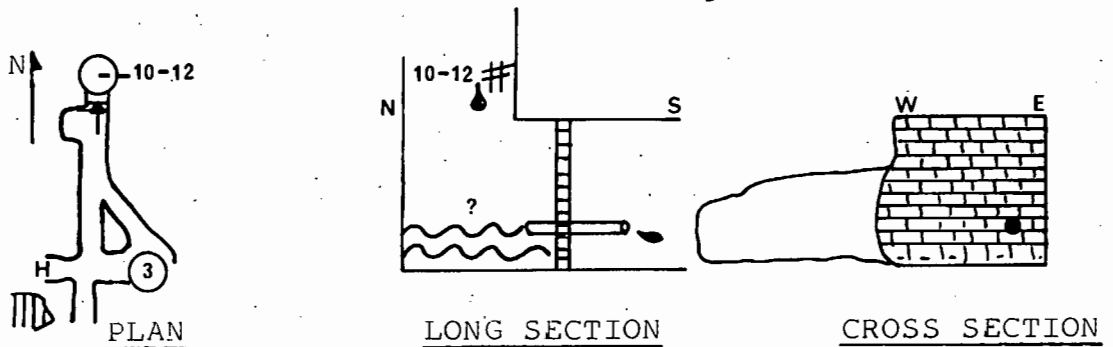
Sample N^o.: 161

Mine Level: 12

Co-ordinates: 1993 E 1973 N Date Sampled: 15 June 1973

Location: At the end of the long drive to the north to the old 10-12 shaft, which is now blocked off by a wall.

Description: A 3m long galvanised pipe emerging from the brick wall closing off the drive.



TCL Borehole N^o.: -

Type: -

Length: - Dip: -

Azimuth: -

Core Size: -

Date of Origin: Min. 10 years old

Purpose: Drains the blocked off area behind the wall.

Water intersected at: -

Yield: -

Geology Etc.: The water is probably coming down the old 10-12 shaft from various higher levels.

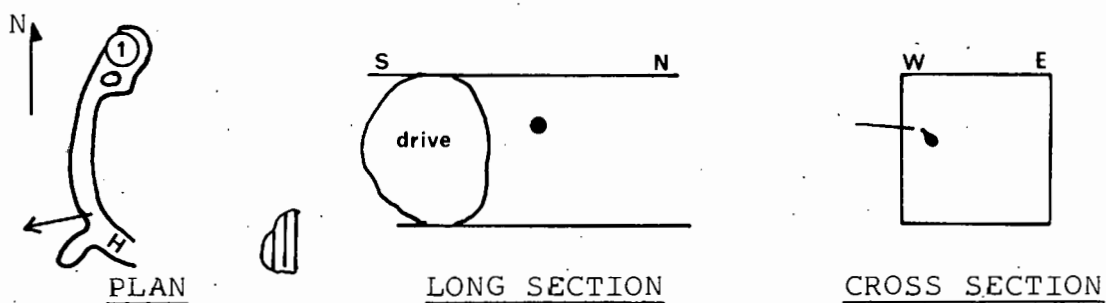
The stream cannot be traced, as it originates in areas of the mine now inaccessible.

APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:
 Technical Data for the 36 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

Sample N^o: 162 Mine Level: 16
Co-ordinates: 1890 E 1853 N Date Sampled: 15 June 1973
Location: On the right hand corner of the first bend
 in the long drive from 1 shaft, just before
 the first short drive to the right.
Description: A single, cased borehole about 2m from the
 ground.



TCL Borehole N^o: H140 Type: Diamond drill
Length: 241 m Dip: +5^o Azimuth: 253^o
Core Size: AX (49,2 mm) Date of Origin: About 1952
Purpose: To investigate the De Wet shaft area at this
 level prior to shaft sinking.

Water intersected at: . - Yield: -

Geology Etc.: Drilled away from the orebody. Not near
 known ore. Only Zone seven dolomite
 intersected, no ore or kersantite.

APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:

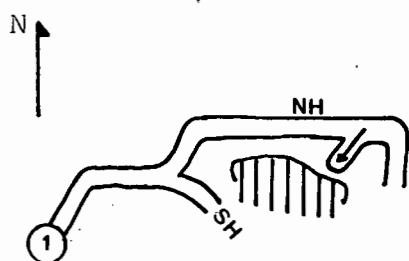
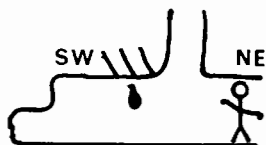
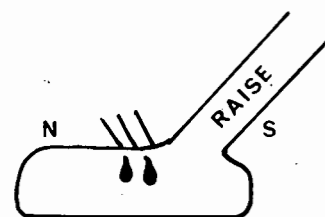
Technical Data for the 36 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

Sample N^o: 163Mine Level: 6Co-ordinates: 2048 E 2051 NDate Sampled: 15 June 1973

Location: Below new exploration raise to upper levels
from a cross cut near the eastern end of the
north haulage.

Description: A leak from fractured rock in the hanging
wall.

PLANLONG SECTIONCROSS SECTIONTCL Borehole N^o: -Type: -Length: - Dip: -Azimuth: -Core Size: -Date of Origin: 1973*

Purpose: Manway exploring low grade upper level ore.
Dormant at time of sampling.

Water intersected at: -Yield: -

Geology Etc.: Above the fracture zone (Zone 6 dolomite),
is pristine moderate grade ore and old
broken fill of fairly good grade. No nearby kersantite, but
fill may contain kersantite rubble from 2 level dyke.

* Although 6 level is half a century old, the raise is
recent.

APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:
 Technical Data for the 36 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

Sample N^o: 164

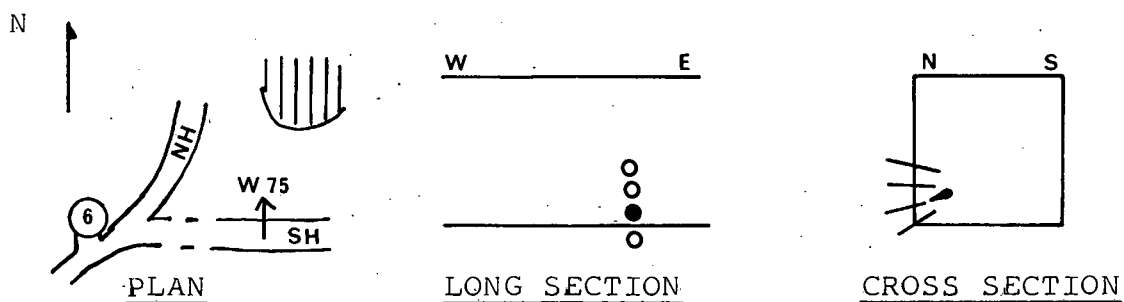
Mine Level: 35

Co-ordinates: 1916E 1821 N

Date Sampled: 19 June 1973

Location: In the north wall of the south haulage, at about
 W 75 section. Within one metre of sample point
 number 135.

Description: One of a group of four cased boreholes in a
 vertical row. One hole is in the floor. 164
 is the lowest of the three holes in the wall.



TCL Borehole N^o: 2760

Type: Diamond drill

Length: 30,5 m Dip: -35°

Azimuth: 024°

Core Size: AX (49,2 mm) Date of Origin: Sept. 1968

Purpose: To test the ore.

Water intersected at: - Yield: -

Geology Etc.: Drilled towards the ore. Moderate mineral-
 isation from 11,3 to 24,4 m (mainly Cu &
 Pb sulphides and oxides). The ore was pristine at the
 time of sampling.

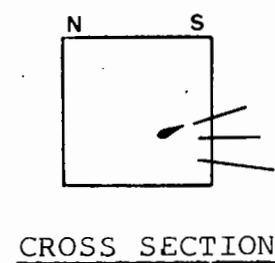
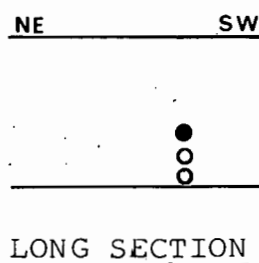
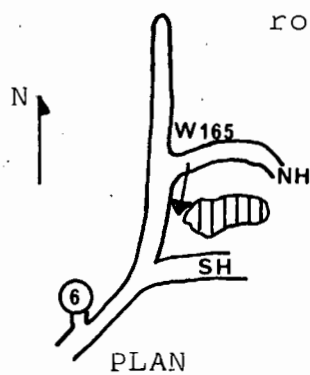
APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:
 Technical Data for the 36 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.

Sample N^o: 165 Mine Level: 33
Co-ordinates: 1856E 1909N Date Sampled: 19 June 1973
Location: South wall of north haulage, on W165 section,
 just east of the long drive to the north.

Description: Topmost of three boreholes in a vertical
 row.



TCL Borehole N^o: 2796 Type: Diamond drill
Length: 54,9 m Dip: + 15° Azimuth: 204°
Core Size: AX (49,2 mm) Date of Origin: Dec. 1968
Purpose: To test the ore.

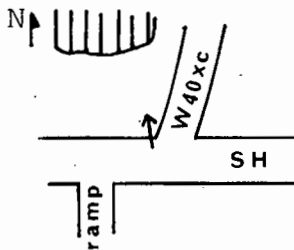
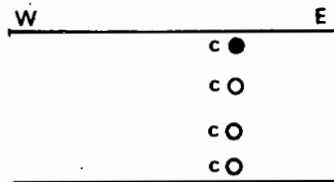
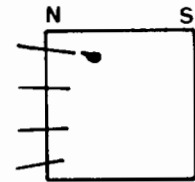
Water intersected at: - Yield: -

Geology Etc.: Siliceous dolomite, with ore zone from
 24,4 m to 36,6 m : moderate grade ore,
 mainly tennantite & pyrite, with subordinate galena
 & sphalerite. Ore was pristine at time of sampling.

APPENDIX A

TSUMEB MINE WATER ORIENTATION SURVEY:

Technical Data for the 35 sampling points.

KEY TO SYMBOLS ETC. ON PAGE 1 OF APPENDIX.
-----Sample N^o: 166Mine Level: 33Co-ordinates: 1937 E 1796 N Date Sampled: 19 June 1973Location: In the north wall of the south haulage, 30 m east of the ramp raise* down to sublevel, on the western corner of W 40 XC.Description: Uppermost of four cased boreholes in a vertical row. Bottom three cemented closed. Has two bolts driven into it. Near roof.PLANLONG SECTIONCROSS SECTIONTCL Borehole N^o: 2549Type: Diamond drillLength: 70,7m Dip: + 40°Azimuth: 024°Core Size: AX (49,2 mm) Date of Origin: 1965Purpose: To test the ore.Water intersected at: - Yield: -Geology Etc.: Strongly mineralised dolomite and massive ore. Mineralised from 18,3 to 70,7m. Massive ore from 36,0 - 47,2m and 67,7 - 70,1m: mainly sulphidic, chief mineral galena, about 3% Cu, 40-50% Pb & about 10% Zn. Ore was pristine at the time of sampling.

* Ramp raise did not exist at the time of sampling.

APPENDIX B: ANALYTICAL METHODS

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APPENDIX B: ANALYTICAL METHODS

Detailed procedures and supplementary notes

B1. INTRODUCTION

The descriptions of procedures and additional notes in this appendix will provide a basis for judging more closely the meaning and limitations of the analytical data compiled in the text of this thesis. Since the thesis is an exercise in applied chemistry it is assumed that the reader is familiar with the principles of sound analytical practice in general and with the analysis of natural waters in particular. The analytical methods are summarized in one or other of the three main subdivisions of the appendix listed below:

(A). Original methods -Tsumeb mine waters (Section B3).

This contains descriptions of all the analytical methods adopted at the beginning of the study when the mine waters were analyzed. Many of these methods were used without modification for the duration of the study.

(B). Modified methods -Borehole waters (Section B4).

This contains descriptions of any modifications that were made to the original methods and any new methods that were adopted during the second stage of the project when the orientation study of borehole waters was undertaken.

(C). Modified methods -Application phase in the Withdrawal area (Section B5).

This describes modifications made to any of the above methods for the purpose of analyzing samples collected during the application of the hydrogeochemical method in the Kalahari terrane.

B2. SUPPLEMENTARY NOTES ON THE EXPERIMENTAL PROCEDURES

The following notes generally apply to all following subsections of this appendix.

Note 1: Organization of descriptions of methods

The experimental techniques are grouped as follows:

1. Physical measurements (partly or wholly *in situ*)
2. Colorimetric methods
3. Gravimetric methods
4. Volumetric methods
5. Atomic absorption spectrophotometry (AAS)
6. X-ray fluorescence spectrometry (XRFS)

Note 2: Control of experimental error

Water samples are easily contaminated and are generally not very stable. The concentrations of the trace components, in particular, can be changed significantly by minute additions or by the immobilization of a few micrograms of the element on the walls of the sample container. Notes and references dealing principally with the control of experimental error during the *collection* and *storage* of hydrogeochemical samples are given in Chapter 3 and Appendix G. In the following subsections of this appendix there are additional notes and references that relate to experimental control during analysis only. (This is well reviewed by Scott and Ure /165/).

Contamination did not present any insuperable problems. Some pick-up was present for certain elements at levels between 0,1 and about 5 µg/l, but this could be successfully monitored and compensated for by the blank.

Due consideration was given to analytical interferences. Many of the techniques used are standard and in these cases the means of minimizing potential interferences are well documented. Special studies of interferences were made when new or highly modified procedures were developed. These tests comprised: (a) Standard additions spiking /28/ of real and artificial samples (b) recovery tests and precision tests in the presence of suspected interferants (c) in the case of AAS, monitoring of non-atomic absorption with a hydrogen continuum source /1175-6/.

Some of the results of these tests have been included where they are useful.

Note 3: Quality of water

Very pure water was used throughout the analytical work and tap water was avoided almost entirely. At the University of Cape Town double distilled water was obtained continuously from a quartz still. Orren /158/ used this same source of water in his study of trace metals in sea water and he encountered no serious problems with blanks. Nor could the writer detect significant amounts of trace elements in the distillate. At Tsumeb the water used in the laboratories was distilled and then double deionized. There were no ponderable amounts of any of the elements of interest in this water.

Note 4: Quality and storage of reagents

Almost all of the materials used were of Analytical Reagent (AR) grade. Chemicals of lower grades were used only when no AR equivalent was available. All reagents used were in any event checked for the presence of trace elements by running blanks. No serious problems were encountered.

All liquid reagents and standard solutions not in their original

bottles were stored in preconditioned containers made of pyrex glass or polyethylene.

Note 5: Standards

Standard solutions were kept as 1000 mg/l stock solutions in dark glass bottles. Most of these were commercial products (Hopkins & Williams or BDH) but a few were prepared from AR reagents using procedures described by Vogel /15/ and others /9,26-8/. Where possible the stock solutions were acidified to prevent the growth of mould and to minimize precipitation and absorption reactions. Dilute standard solutions were prepared from these stock solutions using pyrex volumetric ware or glass- and plastic micropipette syringes. The apparatus used for preparing solutions with concentrations of less than one milligram per litre was not used for any other purpose. Solutions less concentrated than 10 mg/l were not reused if they were more than 12 hours old. The standards were matched as closely as possible to the samples (pH, ionization buffers etc.). Standards were prepared to span the whole range of observed sample concentrations; i.e. unknown concentrations were never estimated by extrapolation beyond a standard.

Note 6: Voltage stabilization

All of the electrical instruments used had good stability but as an added precaution readings were not made during periods of peak load.

Note 7: Cleaning, categorization and storage of glassware

Glassware was cleaned by soaking in solutions of Tepol or Extran. All glassware was preconditioned by soaking for at least 24 hours in solutions of the liquid reagents that were to be used with the apparatus. For example, measuring cylinders used for solvent extraction were treated with a solution of nitric acid, MIBK, APCD and oxine. Samples of glassware were put through a blank run at the beginning of any developmental work to ensure that pick-up from this source had been reduced to an acceptable level.

The writer found it very advantageous to pay particular attention to the categorization and storage of apparatus used for trace element determinations. All clean glassware was stored in dustfree cupboards on and under plastic sheeting. Glassware used for preparing standards was kept separate from that used with samples. A separate set of pipettes, etc. was maintained for each element. This entailed a great duplication of glassware but it is the writer's opinion that this precaution contributed significantly to the maintenance of low blank values and a reduction of random contamination.

Note 8: Handling of sample aliquots

It was advantageous to keep to a minimum the amount of glassware with which samples and standards came into contact. Aliquots of samples or standards were transferred from one container to another only when this was unavoidable. In AAS determinations, especially, it was often possible to draw aliquots directly from the container in which the sample was stored.

Note 9: Abbreviation of descriptions of methods

The descriptions of step-by-step analytical procedures make mention only of the principal apparatus and operations. There are some notes on particularly bothersome practical problems with obscure or unexpected causes and some hints on useful techniques.

Note 10: Calculation of precision

Precision and accuracy in exploration geochemistry have been adequately discussed by Garrett (1969 /1152/). The analytical values reported in this thesis were, wherever possible, the mean of several readings involving a selected sample. For example, the AAS signal for each aspirated sample was integrated three times to obtain a mean value.

Quantitative precision data are tabulated in appropriate sections of the main text of the thesis and also in some appendixes. Precision was calculated from all the multiple determinations of both standards and samples in any complete analytical run. This therefore included day-to-day variations in reproducibility. The reported precision figures are expressed as the estimated limiting percentage error at the 95% level of confidence. For example, a reported precision of 20% for arsenic at a level of 40 µg/l means that repeated analysis of a sample containing about 40 µg As per litre should yield values within ±20% of the mean value 95 times out of a 100. The precision figures are readily obtained from tables of the area under the Gaussian curve /265/.

Note 11: Detection limit concentrations

The detection limit D is usually defined /28/ as:

$$D = 2SC/X$$

where C is a concentration just above the detection limit and X and S are the mean and standard deviation of the signals or readings obtained. This definition is not always practical for everyday use and in this thesis the detection limit is arbitrarily redefined as 150% of the maximum observed blank reading. It follows that the reported detection limits are generally

somewhat higher than the absolute capabilities of the methods described.

B3. METHODS ORIGINALLY ADOPTED FOR THE EXAMINATION AND ANALYSIS OF SAMPLES COLLECTED DURING THE ORIENTATION STUDY OF TSUMEB MINE WATERS (CHAP.3)

B3.1 General

The determination of manganese, chromium, arsenic, germanium, sulphate, phosphate, total suspended solids (TSS), total dissolved solids (TDS), alkalinity, hardness, chloride, fluoride and, initially, selenium and tellurium was achieved with methods routinely used in the laboratories of Tsumeb Corporation Limited (TCL). These methods are based on published work that is cited in the appropriate subsections of this appendix. Most of the methods involving flame AAS were based on the standard procedures recommended by the manufacturers of the instruments. The determination of mercury, however, made use of a modified form of the method of Hatch and Ott /22/, which was developed by TCL. The procedures involved in AAS analysis by carbon rod atomization were developed by the author from the basic principles of AAS technique.

B3.2 Physical measurements (all *in situ*)

(a) Discussion

The rate of water flow, pH, water temperature and air temperature were all measured *in situ*. The water temperature and pH were measured directly in the flowing stream in all except a few very awkward situations; e.g., the pH meter would not operate properly in some stopes where the humidity was 100% and the temperature exceeded 40°C.

(b) Methods of measurement

Temperature: Glass/mercury laboratory thermometer graduated in steps of 0,1°C.

pH: Pye Unicam 293 meter with Philips CAlI electrode.

Rate of flow: Graduated 20l plastic bucket and stopwatch.

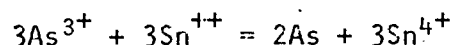
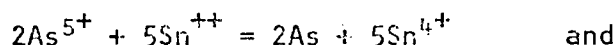
B3.3 Colorimetric methods

(1) ARSENIC

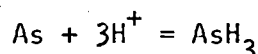
(a) Discussion

This well known method for the colorimetric determination of small amounts of arsenic /10, p.17/ has been slightly modified by TCL /9/.

In strongly acid solutions dissolved arsenic reacts with tin ions /8/:



When metallic zinc is added, nascent hydrogen produces arsine quantitatively:



The arsine forms a coloured complex with silver diethyldithiocarbamate. The reaction may also produce H_2S , PH_3 and SbH_3 , which interfere. These gases are removed by CuCl and lead acetate. A typical working curve is depicted in Fig. B(A). The detection limit varies from 1 to 4 $\mu\text{g/l}$, depending on the reagent blank, which changes with each batch of zinc granules.

(b) *Apparatus and reagents*

Special arsine generator, Fig. B(B); clean and dry, joints well sealed with silicone grease.

Beckmann DU Quartz Spectrophotometer. (Sets of matched cells were used for all colorimetric measurements).

HCL AR concentrated (conc.)

KI solution (soln.) 15 g AR KI per 100 ml water

SnCl_2 soln. 40 g AR $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ per 100 ml water

Zn AR finely granulated metal

Lead acetate soln. 10 g $(\text{CH}_3\text{COO})_2\text{Pb} \cdot 3\text{H}_2\text{O}$ per 100 ml water

CuCl ($=\text{Cu}_2\text{Cl}_2$) soln. Saturated soln. in AR ethanol

Silver diethyldithiocarbamate soln. 0,5 g of reagent per 100 ml pyridene

Acetate plug Glass wool soaked in lead acetate soln. and dried

CuCl plug Glass wool soaked in CuCl soln. and dried. (Keep dry).

(c) *Procedure*

Into the delivery tube: 5 g acetate plug; 5 g CuCl plug.

Into collection tube: 5 ml pyridene-silver diethyldithiocarbamate soln.

Into Erlenmeyer flask in *fume cupboard*: 50 ml sample. 5 ml HCl. 2 ml KI.

8 drops SnCl_2 . Stand for 30 minutes. 5 g Zn via a funnel. Replace delivery tube immediately to avoid loss of arsine. Cool if the reaction is too vigorous. Allow to evolve for 30 minutes. Measure colour of pyridene soln. against standards at 525 nm with slit = 0,04 mm and the filter out.

(2) GERMANIUM

(a) Discussion

This standard method for the colorimetric determination of germanium /11,29/ has been modified by TCL /9/. This modification is suitable only for dilute aqueous solutions of germanium that are fairly free of interfering ions. In the presence of oxygen Ge(IV) is rapidly formed in solution and so as a rule this is the oxidation state of germanium in aerated natural waters /12/. Ge(IV) reacts with HCl to give GeCl_4 , which forms a coloured complex with phenylfluorone (XV) (alias 9-phenyl-2,3,7-trihydroxy-6-fluorone or 2,3,7-trihydroxy-9-phenylxanthen-6-one /13/). This complex is very specific for germanium and the determination can be carried out in dilute solutions of other metals /14/. At high concentrations, As, Sn and Sb may interfere /13/ but none of these elements is present in significant amounts in Tsumeb mine water (Chapter 3, Results). As the Ge-phenylfluorone complex is a colloid, Gum Arabic is added to prevent precipitation. The working curve obtained is similar to that of arsenic and the detection limit is about $3 \mu\text{g/l}$.

(b) Apparatus and reagents

Beckmann DU Quartz spectrophotometer

Gum Arabic soln. Prepare freshly. 2,5 g gum in boiling water. Cool. Filter through cotton wool. Dilute to 500 ml with water.

Phenylfluorone soln. 0,45 g of reagent in 2850 ml AR ethanol, 43,6 ml 1:1 H_2SO_4 and 106,4 ml water. Age for 24 hours. Store in a refrigerator (5°C)

HCL 5,3N

Hydroxylamine hydrochloride soln. 20% w/v in water

(c) Procedure

Place 10 ml sample in 50 ml volumetric flask. 2 ml water. 9,9 ml HCl. 2,5 ml hydroxylamine hydrochloride. 5 ml Gum Arabic soln. Shake. Stand 5 minutes. 15 ml phenylfluorone soln. Make up to 50 ml with water. Shake. Stand for 30 to 120 minutes. Measure colour at 510nm; slit = 0.06 mm ; filter out, against standard solutions of germanium.

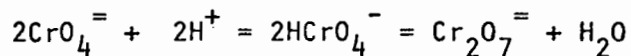
(d) Note: Preparation of germanium standards

Do not, as is advised in some texts, dissolve germanium or its compounds in HCl. This is frankly stupid, since germanium chloride is very volatile.

(3) CHROMIUM

(a) Discussion

This widely used method /10, p. 20/ & /15/ has been slightly modified by TCL /9/. It is a reliable procedure for small amounts of chromium in natural waters. The metal undergoes alkaline oxidation to $\text{CrO}_4^{=}$. When the solution is acidified $\text{Cr}_2\text{O}_7^{=}$ is stabilized:



This gives a violet complex with diphenylcarbazide. Iron interferes if present in large amounts but in Tsumeb mine water iron is virtually absent (Results, Chapter 3). A straight, almost blank-free working curve is obtained.

(b) Apparatus and reagents

Beckmann DU Quartz spectrophotometer

NaOH soln. NaOH AR, 15% w/v in water

Bromine water Saturated

H_2SO_4 AR conc.

H_2SO_4 soln. 5%

Diphenylcarbazide soln. 0,1g in 50 ml AR acetone and 50 ml water

(c) Procedure

Place 100 ml sample in a 400 ml beaker. 0,5 ml NaOH soln; the pH should exceed 10 and any magnesium present will precipitate. 10 ml bromine water (*fume cupboard*). Stand 30 minutes. 5 ml dilute H_2SO_4 . Boil down to 20-30 ml. Cool. Transfer quantitatively to a 50 ml volumetric flask. 2 ml diphenylcarbazide. Make up to the mark with water. Shake. Stand 5 minutes. Read against standards of chromium at 540 nm; slit = 0,02 mm; filter out.

(4) MANGANESE

(a) Discussion

This widely-used method /10, p. 29/ & /15/ has been slightly modified by TCL /9/. Manganese is oxidized to MnO_4^- by KIO_4 and the coloration due to the permanganate ion is measured. Perchloric acid removes interfering organic matter. Digestion with nitric and sulphuric acids removes interfering chloride. Phosphoric acid is added to complex

interfering Fe(III). This is a reliable method for the determination of small amounts of manganese in natural waters. A straight working curve with a slight blank is obtained.

(b) *Apparatus and reagents*

Beckmann DU Quartz spectrophotometer

HClO_4	AR conc.
HNO_3	AR conc.
H_2SO_4	AR conc.
H_3PO_4	AR conc.
KIO_4	AR

(c) *Procedure*

Place 100 ml sample in a 400 ml beaker. 3 ml HClO_4 . Fume to dryness. Cool slightly. 5 ml HNO_3 , 5 ml H_2SO_4 . Fume until dense white fumes are evolved and then for a further 30 minutes. Cool slightly. 5 ml H_3PO_4 and 75 ml water. 0,4 g KIO_4 . Boil for 10 minutes, leave next to hot plate for 20-30 minutes. Cool. Transfer quantitatively to a 100 ml volumetric flask and make up to the mark with water. Shake. Read against standard solutions of manganese at 530 nm; slit = 0,03 mm; filter out.

(5) *PHOSPHATE*

(a) *Discussion*

This is a standard method for the determination of total dissolved phosphate; i.e., meta- and ortho-phosphate /10, p. 26/, which has been modified slightly by TCL /9/. The phosphate complexes are hydrolyzed with sulphuric acid. Ammonium molybdate forms a quantitative complex with PO_4^{3-} at room temperature. This can be quantitatively reduced to a more stable, blue complex by the action of SnCl_2 . A straight working curve with a slight blank is obtained. Great care must be taken to avoid contamination from detergents etc. that contain phosphate.

(b) *Apparatus and reagents*

Beckmann DU Quartz spectrophotometer

HCl	AR conc.
H_2SO_4	10N
SnCl_2	Prepare daily. 0,2 g in 100 ml volumetric flask containing 1 ml conc. HCl and 5 ml water. Make up to the mark with water and shake.

Ammonium molybdate soln. 32 g in a mixture of 150 ml water and 250 ml 10N H_2SO_4 . Dilute to 500 ml with water.

(c) *Procedure*

Place 100 ml of sample in a 400 ml beaker. 10 ml H_2SO_4 . Boil until the volume is less than 50 ml. Cool and transfer quantitatively to a 100 ml volumetric flask. 10 ml molybdate soln. Shake. 5 ml $SnCl_2$ soln. Make up to the mark with water. Shake. Stand for 15 minutes. Read against phosphate standards at 700 nm; slit = 0,03 mm; filter in.

(6) *SELENIUM AND TELLURIUM*

(a) *Discussion*

TCL /9/ has modified the original method described for the determination of selenium and tellurium in natural waters /16/. Both elements are determined in the same aliquot. The method is tedious and taxing. The reagents are unstable and toxic or carcinogenic. The tellurium complex is very sensitive to light. The method is relatively unreliable for concentrations of selenium and tellurium below 1 mg/l. The method was used only in the preliminary investigations of the Tsumeb mine water and was replaced almost immediately by the AAS methods described in B3.7 and especially B4.4. The AAS methods are strongly recommended in preference to this colorimetric method.

Selenium and tellurium are co-precipitated with arsenic and thus separated from any interfering metallic ions. The precipitate is dissolved. Arsenic does not interfere. Selenium is complexed with diaminobenzidine hydrochloride and extracted into toluene. Tellurium is complexed with sodium diethyldithiocarbamate and extracted with chloroform. For either element a straight working curve with a slight blank is obtained.

(b) *Apparatus and reagents*

Millipore HAWP 04700 cellulose filters and an appropriate vacuum filtration system

Separating funnels and stands

pH meter and electrode

Zeiss Elko II spectrophotometer

Sodium arsenite soln. *Extremely toxic*. 0,25 g AR arsenious oxide and 10 pellets of AR NaOH in 10 ml water. Dilute to 200 ml with water.

Sodium hypophosphite soln. 50% w/v in water

HCl	AR conc.	
HCl	1:1	
HNO ₃	AR conc.	
HClO ₄	AR conc.	
EDTA soln.	2% w/v EDTA (Titriplex III, Merck) in water	
Formic acid	10%	
3:3'diaminobenzidene HCl (<i>carcinogenic</i>)	0,01 g in 5 ml water	
NH ₄ OH	1:1	
Toluene	AR	
Na ₂ SO ₄	AR	
KCN soln.	(<i>exceedingly toxic</i>)	5% w/v in water
Sodium diethyldithiocarbamate	Prepare daily.	1 g in 100 ml water
Chloroform	AR	

(c) *Procedure*

Place 100 ml sample in a 400 ml beaker. 50 ml conc. HCl. 4 ml arsenite soln. 25 ml hypophosphite soln. Boil gently for 5 minutes. Filter through a millipore disc, rinsing beaker and disc thrice with 1:1 HCl. Discard filtrate. Transfer disc and contents to the original beaker. 5 ml HNO₃, 2 ml HClO₄. Heat until fumes are evolved. Cool. Transfer quantitatively to a 50 ml volumetric flask and make up to the mark with water. Shake.

(i) For selenium

Pipette 25 ml from the volumetric flask into the original beaker. 5 ml EDTA soln. 2 ml formic acid. Adjust pH to 2,5 with 1:1 NH₄OH. Wash the electrode with a minimum of water. 5 ml diaminobenzidene hydrochloride soln. Stand for 50 min. Adjust pH to 6-7 with 1:1 NH₄OH. Rinse electrode with a minimum of water. Transfer to a separating funnel. 20 ml toluene (burette). Shake vigorously for 30 seconds. Allow to separate and discard the aqueous phase. Run toluene phase into a 100 ml Erlenmeyer flask containing 1g anhydrous Na₂SO₄ to dry the toluene. Swirl. Read immediately using the Elko II with a S42E filter, against blanks and selenium standards.

(ii) For tellurium

Rinse the remaining contents of the 50 ml flask into a 250 ml beaker with water. Reduce to 2 ml by heating. Cool. 2 ml conc. H₂SO₄. Fume down to 1 ml. Cool. 25 ml water. Adjust pH to 7 with 1:1 NH₄OH. Rinse electrode with a minimum of water. 5 ml KCN soln. (*Do not add cyanides to solutions with a pH less than 7. Hydrogen cyanide may be evolved*). Adjust pH to 8,5 with 1:1 NH₄OH. Rinse electrode with a minimum of water. Transfer quantitatively to a separating funnel. Now operate in near dark conditions. 2 ml sodium diethyldithiocarbamate soln. 20 ml chloroform from

a burette. Shake vigorously for 30 seconds. Run chloroform phase into a 100 ml Erlenmeyer flask painted black and containing 1 g anhydrous Na_2SO_4 . Swirl. Read immediately using the S42E filter against a blank and standard solutions of tellurium.

B3.4 Gravimetric methods

(1) *Sulphate*

(a) *Discussion*

The standard gravimetric method for sulphate /15, p.462/ is used with slight modification by TCL /9/. Sulphate is precipitated as barium sulphate. There are small errors (<3%) due to co-precipitation but these can be ignored in exploration studies. Precision data for the gravimetric determination of sulphate are given in Table B3.4 and additional information can be found in subsection B4.

(b) *Apparatus and reagents*

Crucibles with bottoms of scintered glass (fine; N^o 4)

Vacuum filtration equipment

HCl 1:1

BaCl_2 soln. 10% w/v

(c) *Procedure*

Place 100 ml filtered sample in a 600 ml beaker. Dilute to about 250 ml. 5 ml HCl. Boil and add, while stirring, 10 ml very hot BaCl_2 soln. Stand until cold. Vacuum filter into a pre-weighed scintered glass crucible. Dry at 110°C. Cool in a desiccator. Weigh. (Clean crucible in 5% EDTA soln.).

(2) *Total suspended solids*

(a) *Discussion*

This is a simple filtration and weighing of the suspended matter of diameter greater than 0,45 μm /9/ & /10, p.11/. A blank is necessary as the millipore discs loose a small fraction of their mass during washing.

(b) *Apparatus*

TABLE B3.4

Multiple determination of sulphate in a bulk sample of Tsumeb mine water

Number of analysis	Sulphate, mg/l
1	453
2	452
3	453
4	449
5	453
6	453
7	453
8	453
9	453
10	454

Mean = 452,6

S.D. = 1,35

%S.D. = 0,298

Vacuum filtration equipment for use with Millipore discs
 Millipore HAWP04700 filter discs

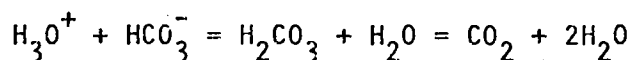
(c) *Procedure*

Measure 500 ml of the agitated sample through a pre-weighed filter disc. Wash with cold, distilled water. Dry at 100°C. Cool in a desiccator and weigh. Use distilled water for the blank.

(3) *Total dissolved solids*

(a) *Discussion*

The method used by TCL /9/ is based on the well-known standard method /10, p.11/. A simple evaporation and weighing is performed. This may not be a very reliable indication of the true mass of dissolved solids in a bicarbonate-rich water because of the loss of carbon dioxide during evaporation:



The residual salts are usually highly hygroscopic and weighing them accurately in a humid climate - such as Tsumeb in summer - can be very difficult without special equipment (which was not available). For detailed comment on this problem see subsection B3.9.

(b) *Apparatus*

Nickel dishes

Drying oven

(c) *Procedure*

Pipette 50 ml of filtered sample into a clean, dry, pre-weighed nickel dish. Evaporate carefully to dryness in a dust-free environment on a hotplate. Dry in an oven at 110°C for 30 minutes. Cool in a desiccator and weigh. (Clean the dishes with dilute hydrochloric acid).

B3.5 Volumetric methods

(1) *Chloride*

(a) *Discussion*

This is the standard argentometric titration /9/ & /15, p.260/. Interference from iodate or chromate is negligible in natural fresh water.

(b) *Reagents*

Potassium chromate indicator soln. 5% w/v in water
Silver nitrate soln. 0,0171N = 2,906 g/l AgNO₃ AR

(c) *Procedure*

Place 20 ml of sample in a beaker. Titrate to the first sign of orange-brown with AgNO₃ soln. This endpoint may be difficult to see if the concentration of calcium is high. Use distilled water for a blank titration.

(2) *Alkalinity*(a) *Discussion*

The TCL method /9/ is based on very well-known procedures /17, p.50/. The theory of alkalinity titrations has been set out in detail by Loewenthal /23/ and others /17, p.47/. For additional information see Appendix I and subsection 4.5 of the main text.

The same aliquot of sample is titrated with dilute sulphuric acid to two consecutive endpoints using two different indicators. These are termed the P and M points and they correspond to the pH_b and pH_a points on the pH-log concentration diagram for dilute aqueous carbonate solutions. Certain important equivalences hold at these points:

P (phenolphthalein) point $\text{pH} \approx 8,3$; $[\text{HCO}_3^-] = [\text{H}^+]$; pH_b

M (methyl orange) point $\text{pH} \approx 4,0$; $[\text{H}_2\text{CO}_3] = [\text{CO}_3^{=}]$; pH_a

The symbol M is retained although better indicators have now replaced methyl orange. The amounts of acid used in attaining these two pH points define the P and M alkalinities of the sample and are calculated from the expressions

$$1000 T_p/\text{sample volume} = \text{P value (mg/l CaCO}_3\text{)} \quad \text{and}$$

$$1000 T_m/\text{sample volume} = \text{M value (mg/l CaCO}_3\text{)}$$

where T_p is the volume of acid required to reach the P point and T_m is the *total* volume of acid required to reach the M point; i.e., including the P titre. From these two values the concentrations of OH^- , CO_3^{2-} and HCO_3^- can be calculated /17/ (Table B3.5). There are certain possible interferences:

(i) Variations in temperature. Provided the difference between the temperature at the time of collection and the temperature at the time of analysis is not very great, this error may be neglected /23/.

(ii) Other weak acid or base systems such as nitrogen acids, ammonia, phosphate, borate, cyanide or organic acids can displace the equilibrium pH values. There are negligible amounts of nitrogen acids, phosphate and cyanide in Tsumeb mine water (TMW) /52/. (cf. concentrations of phosphate reported in Chapter 3). The amounts of ammonia, borate and organic acids in TMW are not yet known but are probably very low /52/.

(iii) The carbonic equilibria are dependent upon the total ionic strength of the solution, which is a function of the mass of dissolved solids present. The variations in TDS found in the samples of TMW (Chapter 3) may be expected to introduce errors of the order of 10% /23/. The discussion of the method of correcting for the effects of ionic strength and related influences is lengthy and has been placed separately in Appendix I.

(iv) Any loss of carbon dioxide from the sample between sampling and analysis will affect the solution equilibria. This process is slow in sealed containers. The data of Appendix I and subsection 4.5 show that the TMW samples were not significantly altered as a result of the loss of carbon dioxide.

It is improbable that the net error resulting from the abovementioned causes will be very serious in the case of natural fresh waters.

(b) *Reagents*

Phenolphthalein indicator 0,5 g of reagent in water. Filter if necessary
 Mixed indicator 0,02 g methyl red and 0,1 g bromocresol green
 in 100 ml ethanol

Sulphuric acid stock soln., 1N Dilute the contents of a 1N H_2SO_4 Titrisol accurately to one litre in a volumetric flask. Prepare monthly.

Sulphuric acid working soln., 0,02N Dilute 20 ml of the stock soln. accurately to one litre in a volumetric flask. Prepare when required.

(c) *Procedure*

The samples should be stored in sealed, full containers. Once sample aliquots are removed from the bottle they should be titrated as rapidly as possible.

TABLE B3.5: RELATIONSHIP BETWEEN ALKALINITY AND THE CONCENTRATIONS OF CARBONIC SPECIES /17, pages 47-50/

(1) ALKALINITY RELATIONSHIPS, mg/l CaCO₃

	[OH ⁻]	[CO ₃ ⁼]	[HCO ₃ ⁻]
P = 0	0	0	M
P = <½M	0	2P	M-2P
P = ½M	0	2P	0
P = >½M	2P-M	2(M-P)	0
P = M	M	0	0

(2) ALKALINITY RELATIONSHIPS, mg/l OH⁻, CO₃⁼ & HCO₃⁻

	[OH ⁻]	[CO ₃ ⁼]	[HCO ₃ ⁻]
P = 0	0	0	$\frac{(M)\text{ml} \times 0,02 \times 61 \times 1000}{\text{sample volume}}$
P = <½M	0	$\frac{(2P)\text{ml} \times 0,02 \times 30 \times 1000}{\text{sample volume}}$	$\frac{(M-2P)\text{ml} \times 0,02 \times 61 \times 1000}{\text{sample volume}}$
P = ½M	0	$\frac{(2P)\text{ml} \times 0,02 \times 30 \times 1000}{\text{sample volume}}$	0
P = >½M	$\frac{(2P-M)\text{ml} \times 0,02 \times 17 \times 1000}{\text{sample volume}}$	$\frac{(2M-P)\text{ml} \times 0,02 \times 30 \times 1000}{\text{sample volume}}$	0
P = M	$\frac{(M)\text{ml} \times 0,02 \times 17 \times 1000}{\text{sample volume}}$	0	0

(i) Phenolphthalein alkalinity - P value

Pipette 100 ml of sample into a 250 ml beaker. Add 3-4 drops phenolphthalein indicator and titrate with 0,02N sulphuric acid until the pink colour just disappears. Record the titre T_p . If the addition of the phenolphthalein does not turn the water pink then the P value is zero; proceed with the determination of the M value.

(ii) Methyl orange alkalinity - M value

To the same aliquot used for determining the P value add 3-4 drops of mixed indicator and continue the titration with 0,02N sulphuric acid until the appearance of the first definite red tinge. Record the total titre, including the value of T_p , as T_m . In both titrations blanks are negligible.

(3) Hardnesses: Total, magnesium and calcium

(a) Discussion

The methods described here are those of TCL /9/ and others /17-8/. In determining total hardness, the mass of all species capable of complexing with EDTA is determined:

$$[Mg^{++}] + [Ca^{++}] + \Sigma[M^{n+}] = \text{total hardness}$$

where the third term represents the sum of all other combining species, such as Fe^{++} . The comprehensive analysis of TMW reported in Chapter 3 shows that the sum of other species is negligible when compared to the concentrations of calcium and magnesium. In determining calcium hardness the pH of the sample aliquot is raised to greater than 13, whereupon almost all of the magnesium is precipitated. Calcium is effectively the only ion left to combine with EDTA. It follows that magnesium hardness is the difference between the total hardness and the calcium hardness.

(b) Reagents

Buffer tablets	Merck Art. 8430, Indikator-Puffertabletten
NH_4OH	conc., chemically pure
EDTA soln.	Contents of a 0,1M Titriplex III Titrisol in 1 litre of water. Store in polyethylene.
NaOH	15% w/v
Mixed indicator	0,2 g calcien, 0,2 g thymolphthalein, 20 g NaCl AR

(c) Procedure

(i) Total hardness

Pipette 20 ml of sample into a beaker. Add about 30 ml water. One buffer tablet. 3 ml NH_4OH . Shake to dissolve. Titrate with EDTA from red to green.

(ii) Calcium hardness

Pipette 20 ml of sample into a beaker. Add about 30 ml water. Add a few drops of NaOH soln., until a white precipitate forms or the pH exceeds 13 (indicator paper). Add some grains of mixed indicator. Titrate with EDTA from a fluorescent yellow-green to a non-fluorescent purple colour.

B3.6 Potentiometric methods

(1) Fluoride

(a) Discussion

Fluoride ion is easily and selectively determined in dilute aqueous solution in the presence of other ions by direct measurement of the activity of the F^- ion with a specific ion electrode /9,19/. The sample is first suitably buffered.

(b) Apparatus and reagents

Calomel electrode Orion 5102090

Orion fluoride specific ion electrode, single junction reference, model 90-01
(These two electrodes are generally mounted together as one unit).

Orion Ionalyzer specific ion meter model 404

Plastic containers for samples and standards: The ones used for standards should have good lids to prevent evaporation (The standards will be stable for at least a week). The containers should have necks wide enough to admit the electrodes. Do not use glass containers, as they rapidly introduce small amounts of fluoride into the solutions.

NaF AR

Glacial acetic acid AR

NaCl AR

NaOH soln. 5M

Disodium CDTA soln. CDTA is cyclohexylenedinitrilotetraacetic acid, alias 1,2-diaminocyclohexane N,N,N',N'-tetraacetic acid. Dissolve 36 g CDTA in 200 ml 1M NaOH soln. to make a stock soln. of the disodium salt. Warm to clear the solution.

Total ionic strength adjustment buffer (TISAB) soln. This can be bought

ready made as Orion solution 94-09-09, or made as follows: 500 ml water in a one litre beaker. 57 ml glacial acetic acid. 58 g NaCl. 4 g disodium CDTA (= 20 ml of the stock soln.). Stir to dissolve. Place the beaker in a bath of cold water and insert a pH electrode. Slowly and with stirring add 5M NaOH soln. until the pH is 5,0-5,5. Cool to room temperature. Transfer quantitatively to a one litre volumetric flask and make up to the mark with water.

Standard fluoride solutions Simple aqueous standard solns. made from NaF; 10^{-3} M, 10^{-4} M, 10^{-5} M and 10^{-6} M.

Buffered fluoride standards Prepare buffered standard solutions, according to the expected concentrations of fluoride ion in the samples, as follows:

10^{-3} M buffered standard = 50 ml 10^{-3} M NaF standard + 50 ml TISAB

10^{-4} M buffered standard = 50 ml 10^{-4} M NaF standard + 50 ml TISAB etc.

(The samples are also diluted 50/50 with TISAB, so that a direct comparison can be made between the samples and the NaF molar standards).

(c) Procedure

In the following discussion the term "the electrode" means both the fluoride and calomel electrodes mounted as one unit. Pipette 50 ml of sample into a *plastic* container. Add 50 ml TISAB soln. Choose two buffered standards spanning the expected molar concentration of F^- in the sample. In the following illustration it will be assumed that the concentration of fluoride in the sample is about 5×10^{-4} and that the meter is being calibrated with standards of 10^{-3} M and 10^{-4} M. Place the electrode in the 10^{-3} M buffered standard. Allow 10 minutes for equilibration and then set the needle of the ion meter to the centre of the scale (100), using the calibration knob. Remove and wash the electrode and dry it with a tissue (It is assumed that this is done between any two immersions of the electrode). Place the electrode in the 10^{-4} M buffered standard solution. The needle will swing towards the left. Allow about 15 minutes for equilibration (The time required for equilibration increases for progressively weaker solutions of fluoride ion but is also dependent upon the age of the electrode. At 10^{-6} M equilibration can take up to 30 minutes. Equilibrium is reached when no significant movement of the needle occurs within a period of 5 minutes). After equilibration, set the needle exactly to 10, using the temperature correction knob. Measure the temperature of the solution and adjust the slope control to this value. The meter is now set to read directly the concentrations of buffered fluoride solutions of between 10^{-3} M and 10^{-4} M on a logarithmic scale. Immerse the electrode in the buffered sample and read the value on the scale at equilibrium. Note that the scale continues

to the right of centre, which in this example is set at $10^{-3}M$, so that concentrations of up to $10^{-2}M$ can be read without recalibrating the instrument. If the needle goes off scale for any sample then the meter must be recalibrated using a more appropriate pair of buffered standards. When the electrode is not in use it should be stored in distilled water.

B3.7 Atomic absorption/emission spectrophotometric methods

B3.7.1 INTRODUCTION

The principles and techniques of AAS and related spectrophotometric methods are very well documented /24-8,174,243-52,266/. Twenty trace elements were analyzed by the writer in three separate runs: (i) Mercury, by a cold vapour method, immediately after collection of the samples. (ii) Zn,Cd,Au,Fe,Cu,Ag,K,Rb,Sr,Al,Si,Li,Na and Cs at the Department of Geochemistry at UCT, using a Varian AA6 instrument /174/, and (iii) Mo, V,Tl,Sb and Bi somewhat later, in Tsumeb, using a Perkin Elmer 303 instrument /26/. Details concerning the storage, handling and transportation of these samples are given in Appendix G.

It should be noted that the literature of AAS has many conflicting statements about interferences /28,266,1207/. In particular, many interferences reported before 1966 are erroneous; they resulted from a reduction of the AA signal by molecular band emission or other emissions in unmodulated spectrophotometers /266/. Both of the abovementioned instruments are modulated /266-7/. Furthermore, many stated interferences are practically insignificant in natural fresh water. Excellent reviews of the analysis of natural waters are given by Ediger /164/ and Parker /28/.

B3.7.2 FLAME ABSORPTION/EMISSION METHODS

(A) GENERAL

The elements determined with the older PE 303 were preconcentrated by solvent extraction in order to achieve good detection limits. The VT AA6 has a carbon rod analyzer (B3.7.3) but the writer preferred to use the flame wherever possible because it is quicker and simpler and less subject to interferences /28/. The carbon rod was used only when very low detection limits were required and only if the observed levels of interferences were within acceptable bounds. Both methods were used for a few elements that showed a wide range of concentrations in the samples. In these cases a few standards and samples of intermediate composition were

analyzed using both the flame and the rod to ensure that the two sets of results were comparable.

(B) ATOMIC ABSORPTION/EMISSION DETERMINATIONS WITHOUT PRECONCENTRATION

The procedures for basic AA/ES measurements are very well known /266/ and the instrumental parameters are largely standardized /24-8/, except for minor operations required to optimize individual spectrophotometers. The VT AA6 was used for all these determinations and the procedures prescribed by the manufacturers /27/ were followed in all essential detail. Known interferences are generally minor. The most serious is probably the enhancement of silicon by sodium, which was first described by Devine and Suhr /1180/ in 1977, long after the analyses described in this subsection had been performed. Ten mg/l of Na_2O enhances SiO_2 by 1 mg/l at all concentrations of SiO_2 from 1 mg/l to 100 mg/l. Two hundred mg/l of Na_2O enhances 10 mg/l of SiO_2 to an apparent value of 16,5 mg/l. In view of the poor performance of silicon as a pathfinder (Chapter 4) it would have been otiose to apply retrospective quantitative corrections to [Si] for [Na] in this exploration project.

The elements that were determined without preconcentration are listed in Table B3.7.2, which also provides details about the gases used etc.

(C) FLAME AAS DETERMINATIONS AFTER PRECONCENTRATION BY SOLVENT EXTRACTION

(i) General

The preconcentration of trace elements by solvent extraction prior to analysis is widely practised /28,214,239,253/. Two solvent extraction systems were used for the determination of certain trace elements in Tsumeb mine water ; a bromide-ether system for thallium, and an MIBK-APCD system for Mo, V, Sb and Bi. (Note that APCD - ammonium pyrrolidinecarbo-dithioate is the correct name for the substance widely and erroneously known as APDC - ammonium pyrrolidenedithiocarbamate /34/). The modified MIBK-APCD system described here was developed by the writer. Attempts to include Tl in the MIBK system failed, despite the fact that the literature describes the extraction of the element into this solvent when complexed with APDC /28,213/. The two solvent systems are described below.

(ii) MIBK-APCD solvent extraction system for Mo, V, Sb & Bi

(a) Precedents

Since its description in 1955 /237/ APCD has become very

TABLE B3.7.2: Elements determined by simple flame AAS

Zn:	A,b	Cd:	A,b
Au:	A,c	Fe:	A,c
Cu:	A,c	Ag:	A,c
K:	E,L	Rb:	A,L
Sr:	N,L	Al:	N,c
Si:	N	Li:	E,L
Na:	E,L	Cs:	E,L

A Absorption, air-acetylene

E Emission, air-acetylene

N Absorption, nitrous oxide-acetylene

L spiked with 5 000 mg/l La and 5 000 mg/l K or Na to suppress ionization

b carbon rod used for a few samples with very low concentrations of the element. See B3.7.3

c determined by flame methods, despite poor sensitivity, because determination by carbon rod methods were subject to too much interference. (In subsequent phases of this project solvent extraction systems were developed to suppress these interferences and it became possible to use the carbon rod for practically all determinations of trace elements. See subsection B4.).

widely used as a chelating agent in solvent extraction, especially in conjunction with MIBK /28,34,158,243-7,249-52/. Oxine (alias 8-hydroxyquinoline or 8-quinolinol /28/) is another popular chelating agent /253, 255/ that can be used with MIBK /254/. The writer added some oxine to the solvent system described here to enhance the efficiency of extraction.

The extraction of molybdenum and vanadium into MIBK with oxine and/or APCD has been very frequently recorded /28,213,252,254,256-7/. Bismuth and antimony are apparently less commonly sought, but both have been successfully preconcentrated by solvent extraction with MIBK-APCD.

(b) Interferences

Interferences encountered in the AAS determination of molybdenum are well documented /28,247,259-63/. After extraction into MIBK the only elements that are likely to interfere - if they are present in a large excess - are iron and manganese. The highest concentration of manganese detected in Tsumeb mine water was about half a milligram per litre, and iron was always much less abundant than this. Interference tests conducted by the writer showed that the addition of 10 mg/l of iron or manganese had no perceptible effect on the absorption signal from a solution containing 10 µg of Mo per litre.

Little is known about possible interferences during the AAS determination of vanadium /247/. Ammonia can be a problem, but this is practically absent in TMW /52/. Recovery tests were conducted by the writer by spiking samples rich in chloride, sulphate, calcium and magnesium with a few micrograms of vanadium. In all cases the signals obtained from the spiked samples were indistinguishable from those obtained from standards prepared in distilled water.

Interferences in the determination of antimony by AAS are not commonly described. It is known that ten-fold excesses of Al, Ba, Ca, Cd, Cr, Fe, K, Mg, Mn, Mo, Na, Pb, Sr and Zn do not interfere /247,264/. Copper and nickel cause a slight depression of the AA signal but these effects are almost eliminated if a strongly oxidizing air-acetylene flame is used. In any case the concentration of copper in TMW never exceeded 100 µg/l and the amount of nickel was always negligible so it seemed safe to assume that these effects could be ignored. It is reported that "an excess of oxidant in the solution" causes a depression of the Sb signal /27/ but TMW contains very small amounts of oxidants such as nitrate ion /52/.

Bismuth is apparently subject to some molecular absorption interference from the alkali and alkaline earth metals in the air-propane flame /247,260/ but this effect is absent in the hotter air-acetylene flame, in which no substance is known to interfere in amounts less than 10 000 mg/l.

In any case the alkalis and alkaline earths are effectively eliminated because they remain in the aqueous phase during extraction.

Unfortunately, no deuterium lamp was available for the PE 303. Non-atomic absorption could therefore not be monitored in this particular run and it is possible that some of the very weak signals observed were in fact spurious.

(c) Theory and development of the method

No antimony ion is really stable in natural waters because of hydrolysis, but Sb(III) is the species most likely to exist /35/. Bismuth in natural waters is almost always present as Bi(III) /35/. Molybdenum will probably be present as molybdate and vanadium as V(V). The writer's experimentation with various MIBK-APCD-oxine solvent extraction systems showed that Mo(IV), V(V), Sb(III) and Bi(III) could all be concentrated efficiently and reproducibly in one operation at pH 4 in the presence of chlorate ion. The role of the chlorate ion, which acts as a stabilizing agent, is discussed by Koirtzjohann /34/. The extraction process becomes increasingly less efficient at higher pH values but is also not practicable at values much below pH 4 because of the formation of insoluble complexes. It is therefore essential to adjust the pH carefully.

(d) Apparatus and reagents

Standard stock solutions, 1000 mg/l The solutions were selected to match the oxidation state most probably associated with each of the four elements in natural water:

Sb_2O_3 in 25% H_2SO_4

Bi metal in 5% HNO_3 (yields Bi(III) /36/)

Ammonium molybdate, 5% acid soln.

V_2O_5 in dilute sulphuric acid

Dilute working standards Prepared daily by dilution with water

PE 303 AA spectrophotometer

250 ml graduated Pyrex glass measuring cylinders with plastic stoppers

Extran detergent Merck Art. 7555 (for cleaning)

EDTA Merck Titriplex Art. 8416 (1% soln. for presoaking glass)

Automatic magnetic stirrer and Teflon-coated followers

pH meter and glass electrode

MIBK AR, Merck Art. 6146

HNO_3 AR, Merck 60%

Dilute HNO_3 1 part conc. acid to ten parts water
 NH_4OH soln. S.G. 0,91 Prepared weekly by bubbling pure NH_3 into water
 HClO_4 AR conc. Merck
APCD Hopkins & Williams N^o. 153700 (specifically for AAS)
APCD soln. Prepare daily. 0,6 g in 50 ml water
Oxine BDH, Analar. 1 g added to each litre of MIBK. Stable for at least ten days.

(e) Procedure

Place 250 ml sample in a 450 ml glass beaker. 0,5 ml HClO_4 . While stirring, adjust the pH to $4 \pm 0,1$ with NH_4OH . Beware of cross-contamination by the electrode. Transfer to a separating cylinder. 2 ml APCD soln. 20 ml of MIBK. Shake for 5 minutes. The blank and standards are treated identically. Determine the concentration of metals in the organic phase immediately, using standard instrumental conditions /26/, in the following order: Mo, V, Sb, Bi. (The Mo complex is appreciably decomposed within the hour). Aspirate the organic phase directly from the cylinder. Spray the bulk MIBK containing oxine as the zero solution. The vanadium and molybdenum blanks were generally negligible. Small blank values were usually noted for antimony and bismuth.

(iii) *Hydrobromic acid/diisopropylether solvent extraction system for thallium*

(a) Discussion

Thallium has a strong affinity for certain halogen acid/ether solutions. Bromo-ether extraction of thallium was recorded at least 60 years ago /241/ and has frequently been documented /214-9,239-40,242/. It has been shown that for a wide range of molarity of HBr the extraction of Tl(III) into diisopropylether is more than 99,9% efficient.

The method described here was originally recorded by Korenman /240/ but has been slightly modified by TCL /9/. The extraction is performed with 6N HBr and the process is very specific and free of complications. The oxidation state of thallium in natural waters is probably Tl(I) but this is irrelevant because the extraction system oxidizes the element to Tl(III) in both the samples and standards.

The literature often mentions the need to preclean the HBr used with ether in order to remove traces of thallium present, but the element could not be detected in the acid supplied by Merck.

Apparently no interferences have been recorded in the determination of thallium by AAS /28/. The writer found that blanks were negligible and

that the working curves were linear and highly reproducible.

(b) Apparatus and reagents

250 ml Pyrex glass graduated measuring cylinders with plastic stoppers

Standard stock soln. of Tl(I) 1000 mg/l in 5% acid soln.

Dilute Tl standards Prepared daily by dilution with water

HBr Merck Art. 304 47%

Diisopropylether Merck Art. 866

Extran detergent Merck Art 7555 (for cleaning glassware)

EDTA Merck Titriplex Art. 8416 (1% soln. used for presoaking glassware to remove all traces of thallium)

PE 303 spectrophotometer

(c) Procedure

Place 225 ml sample in a cylinder. 25 ml HBr. 10 ml ether. Shake for two minutes. The phases separate very rapidly. Treat blanks and standards identically. Determine Tl in the air-acetylene flame using the standard conditions for the instrument /28/. Aspirate the organic phase directly from the cylinder and use pure ether as a zero solution.

B3.7.3 FLAMELESS ATOMIC ABSORPTION METHODS

(A) *GENERAL*

Described here are the carbon rod atomization techniques used in conjunction with the conventional flame methods described in B3.7.2, and a cold-vapour method for mercury.

Although this section of the appendix was prepared in 1976, it should be noted that the analyses described were performed in 1973, using one of the first commercially produced carbon rod atomizers to arrive in Africa, and without the benefit of the literature on this subject that has since appeared.

(B) *ATOMIC ABSORPTION ANALYSIS USING THE CARBON ROD ATOMIZER*

The carbon rod atomization technique is relatively new. The analysis of water by carbon rod AAS is reviewed by Dolinsek and Stupar /163/. The instrument used for the analyses described here was a Varian Techtron AA6 spectrophotometer with a VT 63 carbon rod accessory. The spectral settings, lamp currents etc. used were those recommended by the manufactures /24-8/.

TABLE B3.7.3 ELEMENTS INVESTIGATED BY CARBON ROD AAS

	a	b	c	d	e	f	g	h	i	j	k	l	sensitivity & detect.lim.	notes
*Fe	8-8	6-5	8-2½	8-8	6-5	6-2½	100µg/l	→0,125;D=4,6µg/l	i,ii					
*Ag				8-8	6-5	6-2½			iii,xii					
*Al	8-8	6-5	8-5	8-8	6-5	8-2½	100µg/l	→0,064	iv					
Pb				8-8	6-5	6-2½		D<1µg/l	v					
**Cd				8-8	6-5	6-2½		D<1µg/l	vi					
*Cu				8-8	6-5	6-2½		D<1µg/l	xii					
Ni	8-8	6-5	5-5	8-8	6-5	8-5	100µg/l	→0,240;D=2,2µg/l	i,ii,iv,vii					
**Zn				8-8	6-5	6-2½	1µg/l	→0,615;D=0,004µg/l	viii					
Te				8-8	6-5	6-2½		D=10µg/l	ii					
Se				8-8	6-5	8-2½		D<1µg/l	ix					
Co				8-8	6-5	8½3	100µg/l	→0,534;D=1µg/l	iv,x					
*Au				8-8	6-5	7-2½	100µg/l	→0,310;D=1µg/l	i					
*Si									iv,xi					

Explanation of letters used in heading:

(a)	decontamination	voltage	drying	stage
(b)	"	time	"	"
(c)	"	voltage	ashing	"
(d)	"	time	"	"
(e)	"	voltage	atomization	"
(f)	"	time	"	"
(g)	operational	voltage	drying	"
(h)	"	time	"	"
(i)	"	voltage	ashing	"
(j)	"	time	"	"
(k)	"	voltage	atomization	"
(l)	"	time	"	"

Explanation of notes:

- (i) continuum or molecular band interference is significant
- (ii) lamp current is 10 ma
- (iii) a standard of 1µg/l is suitable for optimization
- (iv) highly refractory element; difficult to decontaminate the rod
- (v) standards between 10 and 100µg/l are suitable
- (vi) the rod cannot be used for concentrations of more than about 30µg/l
- (vii) the decontamination step is used here to remove volatile interferants
- (viii) problems with the reagent blanks are encountered above the det. lim.
- (ix) the graph of conc. vs. absorbance flattens very rapidly
- (x) lamp current is 8 ma
- (xi) no suitable setting could be found
- (xii) unsatisfactory or poorly reproducible working curve observed. Cause uncertain.

* and ** : see page B 29, first paragraph

The various settings for the operation of the rod itself were determined by the writer in a series of experiments with aqueous standard solutions of each metal. The elements determined or investigated with the carbon rod are listed in Table B3.7.3, together with various technical data. Significant problems of various kinds were encountered with carbon rod analysis of the untreated solutions of the elements marked with a single asterisk, and wherever possible the samples of mine water were analyzed for these elements by flame AAS. A double asterisk identifies those elements that were sometimes too concentrated in the samples to be determined by the carbon rod technique. The sensitivity factors recorded in the table are the absorbances produced by a standard of the stated concentration. The table includes the settings used when decontaminating the rod by firing it between the analysis of any two consecutive samples. Where no decontamination settings are given, none were found to be necessary.

(C) AAS DETERMINATION OF MERCURY BY THE COLD-VAPOUR METHOD

(a) Discussion

The method used by TCL is a variation of the well-known technique in which mercury is reduced to an atomic vapour by the action of stannous chloride /20-2,1160/. The method is sensitive to nanogram amounts of mercury but at these low concentrations the precision is poor and several aliquots of the same sample must be analyzed in order to get a reasonable average value. The poor precision is probably due to absorption at the mercury wavelength by variable amounts of water vapour and other gases. It was not possible to correct for these effects with the equipment described here. (A more sophisticated system was used at a later stage; see subsection B4.).

(b) Apparatus

TCL has constructed a mercury analyzer by modifying a Techtron AAS AR200Cu instrument. The copper lamp was replaced by a mercury lamp and a transparent absorption tube was substituted for the burner. This tube is about 15 cm long. The sample is placed in a glass vial of about 100 ml capacity, through which compressed air can be directed by means of a tap. The air enters through the rubber bung closing the vial via a glass tube that dips below the surface of the sample. A second tube conducts the vapour to the absorption chamber via a cotton wool plug, which absorbs any droplets of water. The sample vial rests on top of a magnetic stirrer and contains a Teflon-coated follower. The instrument is connected to an Hitachi QPD 53 chart recorder.

(c) Reagents

Stannous chloride soln. AR 20% w/v

(d) Procedure

Place 10 ml of sample in the vial containing the magnetic follower. 5 ml SnCl_2 . Seal quickly and start the stirrer. Stir for 60 seconds and then turn on the air tap. Record the absorption peak on the chart recorder and compare the peaks due to the samples with those due to mercury standards of 1 to 100 ng/l.

B3.8 X-ray fluorescence spectrometry- composition of suspended solids

The collection of the suspended matter in samples of Tsumeb mine water was described in subsection B3.4. Some of the millipore discs on which the material was collected were dried and examined by X-ray fluorescence spectrometry. The discs selected for this purpose were either heavily coated with precipitates or were highly coloured- the latter sign perhaps indicating the presence of heavy metals. The analysis was performed in the Dept. of Geochemistry at UCT, using a Philips 1220 instrument /1186/. Table B3.8 lists the experimental conditions. Spectral peaks were registered on a chart recorder. The heights of the peaks were evaluated semi-quantitatively, as follows:

- 0 = no visible peak
- ? = probable slight peak
- 1 = up to 1/3 of total chart scale
- 2 = between 1/3 and 2/3 of total chart scale
- 3 = more than 2/3 of total chart scale

A new millipore disc was used as a blank, because Spencer and Manheim /1188/ have shown that the ash of millipore filters may contain ponderable amounts of Na, Ca, Si, Mg, K, P, Fe, Cu, Cr, Zn and Al.

B3.9 General observations concerning the quality of data for the major components of Tsumeb mine water

(A) *The relationship between the values for TDS determined by two methods*

The mass of dissolved solids in the sample was determined by evaporation and weighing (B3.4). The total amount of dissolved solids (TDS)

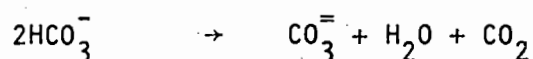
TABLE B3.8 INSTRUMENTAL CONDITIONS FOR SEMI-QUANTITATIVE XRF ANALYSIS OF TSS

	First run*	Second run**
2θ range	18° to 118°	over peaks only
crystal	LiF (200)	PET for Si,Al;ADP for Mg
target	W; 70KV,28ma	Cr; 55KV,36ma
counter	flow & scintillation	flow only
collimator	fine	coarse 550 μm
scanning speed	4° 2θ per minute	4° 2θ per minute
scale factor	4 x 10 ⁴ cps full scale	2 x 10 ³ cps full scale
time constant	0,5	0,5
vacuum	on	on
chart speed	1 600 mm per hour	1 600 mm per hour

* For Ca, Ti, Mn, Fe, Cu, Pb and Zn.

** For Si, Al and Mg.

can also be estimated by summing the masses of all the species determined in each sample. All the important constituents of TMW have been determined and the mass of undetermined species is probably less than 10 mg/l. A comparison of the two independently derived values for TDS therefore provides an estimation of the quality of the analytical data for the major components of these waters. The two estimates are compared in Table B3.9A. Column 2 gives TDS as the sum of all species determined in the sample. Column 3 gives TDS determined gravimetrically. This value must be corrected for the loss of volatiles resulting from the decomposition of bicarbonate during drying. Column 4 is the concentration of bicarbonate in the sample and column 5 is the compensatory mass that must be added because of the reaction



Column 6 is thus the sum of columns 3 and 5. Column 7 is the difference between the two estimates of TDS. This value should be compared to the estimated maximum experimental error involved in the gravimetric determination of TDS, which is given at the foot of the table. Thirteen of the samples exceed these limits of error. They are marked with an asterisk and the amount by which the limits of error is exceeded is given in column 8. Assuming this excess to be due to error in the value of TDS obtained by summation, the percentage error in Σx TDS necessary to generate this excess can be calculated. This is given in column 9. The value is always less than 10% and more than half of the errors are under 5%. The maximum uncertainty in Σx TDS, estimated independently, is about 15%, so the agreement is favourable.

(B) *Ionic balances*

The quality of a total analysis of a water sample is commonly checked by comparing the equivalent masses of the total cationic and anionic populations. In TMW this means comparing calcium, magnesium, sodium and potassium with chloride, sulphate and bicarbonate, since the mass of all other constituents is negligible. Table B3.9B lists the concentrations of these seven species in milliequivalents (meq), and gives the cationic and anionic totals. The mean of these two totals is given in column 11 and the difference between them in column 10. In column 12 this difference is given as a percentage, calculated as $(\text{total cations} - \text{total anions}) \times 100 / (\text{total cations} + \text{total anions})$. The difference is less than 5% in 86% of the samples and reaches a maximum of 7.6%.

TABLE B3.9A COMPARISON OF TWO ESTIMATES OF TDS

sample number	Σx TDS	grav. TDS	$[\text{HCO}_3^-]$ mg/l	mass lost	corrected grav. TDS	TDS diff.	error excess	$\% \Sigma x$ TDS
131	1425	1300	537	273	1573	-148		
132	1594	1700	375	191	1891	-297		
133	1133	1150	531	270	1420	-287		
134	1366	1400	531	270	1670	-304		
135	1315	1200	543	276	1476	-161		
136	1409	1450	546	277	1722	-313		
137	1936	2020	433	220	2240	-304*	44	2,3
138	1536	1440	473	240	1680	-144		
139	924	880	529	269	1149	-225		
140	1577	1560	387	197	1757	-180		
141	1511	1560	477	242	1802	-291*	31	2,1
142	1560	1640	482	245	1885	-325*	65	4,2
143	1626	1680	487	247	1927	-301*	41	2,5
144	1144	900	556	283	1183	-39		
145	1123	1300	295	150	1450	-327*	67	6,0
146	1781	1880	466	237	2117	-336*	96	5,4
147	1183	1220	537	273	1493	-310*	50	4,2
148	1912	2040	428	218	2258	-346*	86	4,5
149	795	560	573	291	851	-56		
150	1386	1220	536	272	1492	-124		
151	1159	960	561	285	1245	-86		
152	852	600	558	283	883	-31		
153	778	520	565	287	807	-29		
154	1339	940	192	98	1038	+301*	41	3,1
155	1897	1860	207	105	1965	-68		
156	1406	1260	538	273	1533	-127		
157	1834	1880	482	245	2125	-291*	31	1,7
158	1745	1840	363	184	2024	-273*	13	0,7
159	1586	1440	543	276	1716	-130		
160	1574	1400	305	155	1555	+19		
161	1344	1100	190	97	1197	+147		
162	831	520	603	306	826	+5		
163	1073	1060	170	86	1146	-73		
164	1129	1180	555	282	1462	-333*	73	6,5
165	1592	1720	519	264	1984	-392*	132	8,3
166	1581	1340	192	98	1438	+49		

Estimated maximum ranges of experimental error in the gravimetric determination of TDS:

Samples 131 to 136: +250 mg/l, -350 mg/l (20 ml sample)

Samples 137 to 166 +220 mg/l, -260 mg/l (50 ml sample)

TABLE B3.9B MILLIEQUIVALENT IONIC BALANCES FOR TSUMEB MINE WATER SAMPLES

sample number	1 Mg ⁺⁺	2 Ca ⁺⁺	3 K ⁺	4 Na ⁺	5 HCO ₃ ⁻	6 Cl ⁻	7 SO ₄ ⁼	8 cat. tot.	9 an. tot.	10 diff. meq.	11 mean	12 diff. %
131	8,1	6,9	0,3	6,0	8,8	4,2	7,3	21,3	20,3	+1,0	20,8	2,4
132	7,1	8,1	0,4	6,5	6,1	6,3	10,5	22,1	22,9	-0,8	22,5	1,8
133	6,3	6,2	0,2	4,2	8,7	2,9	4,0	16,9	15,6	+1,3	16,3	4,0
134	7,5	6,9	0,3	5,6	8,7	4,0	6,7	20,3	19,4	+0,9	19,9	2,3
135	6,7	6,8	0,2	5,0	8,9	3,9	6,0	18,7	18,8	-0,1	18,8	0,3
136	7,9	7,1	0,2	5,5	9,0	3,9	7,3	20,7	20,2	+0,5	20,5	1,2
137	9,5	9,4	0,3	7,7	7,1	8,3	14,9	26,9	30,3	-3,4	28,6	5,9
138	7,8	7,7	0,2	6,2	7,8	6,5	9,5	21,9	23,8	-1,9	22,9	4,1
139	5,9	5,8	0,2	2,0	8,7	1,2	2,2	13,9	12,1	+1,8	13,0	6,9
140	9,4	7,6	0,9	5,4	6,3	3,1	13,5	23,3	22,9	+0,4	22,6	0,9
141	7,3	7,9	0,2	6,2	7,8	6,0	8,8	21,6	22,6	-1,0	22,1	2,3
142	7,5	7,9	0,2	6,4	7,9	6,7	9,1	22,0	23,7	-1,7	22,9	3,7
143	7,2	8,9	0,3	6,1	8,0	4,6	11,5	22,5	24,1	-1,6	23,3	3,4
144	6,6	6,1	0,2	3,6	9,1	2,2	4,5	16,5	15,8	+0,7	16,2	2,2
145	7,7	7,1	0,2	2,7	5,5	1,5	9,2	17,7	16,2	+1,5	17,0	4,4
146	7,7	8,8	0,3	7,0	7,6	7,2	12,7	23,8	27,5	-3,7	25,7	7,2
147	7,2	6,8	0,2	4,3	8,8	2,6	4,5	18,5	15,9	+2,6	17,2	7,6
148	9,5	9,3	0,3	7,5	7,0	8,0	14,8	26,6	29,8	-3,2	28,2	5,7
149	5,3	5,1	0,2	0,7	9,4	0,3	0,4	11,3	10,1	+1,2	10,7	5,6
150	7,6	7,0	0,3	5,2	8,8	3,9	6,9	20,1	19,6	+0,5	19,9	1,3
151	6,9	6,3	0,2	3,8	9,2	2,4	4,2	17,2	15,8	+1,4	16,5	4,2
152	5,3	5,2	0,2	1,2	9,1	1,0	1,1	11,9	11,2	+0,7	11,6	3,0
153	5,0	5,1	0,1	0,4	9,3	0,2	0,5	10,6	10,0	+0,6	10,3	2,9
154	8,4	7,7	0,4	4,7	3,1	3,7	13,1	21,2	19,9	+1,3	20,6	3,2
155	12,1	13,1	0,5	4,1	3,4	2,8	22,0	29,8	28,2	+1,6	29,0	2,8
156	7,4	7,4	0,3	5,5	8,8	4,1	7,1	20,6	20,0	+0,6	20,3	1,5
157	8,8	9,7	0,3	7,1	7,9	6,6	13,3	25,9	27,8	-1,9	26,9	3,5
158	8,0	9,2	0,4	7,2	6,0	7,3	13,7	24,8	27,0	-2,2	25,9	4,2
159	7,8	8,2	0,3	6,1	8,9	4,9	9,5	22,4	23,3	-0,9	22,9	2,0
160	12,8	7,2	0,4	4,1	5,0	2,9	15,6	24,4	23,5	+0,9	24,0	1,9
161	9,5	6,8	0,4	5,0	3,1	3,8	13,3	21,7	20,2	+1,5	21,0	3,6
162	5,8	5,3	0,0	0,1	9,9	0,1	0,9	11,2	10,9	+0,3	11,1	1,4
163	6,0	4,6	0,3	6,0	2,8	4,3	9,0	16,9	16,1	+0,8	16,5	2,4
164	6,1	6,1	0,1	2,3	9,1	2,5	4,8	14,6	16,4	-1,8	15,5	5,8
165	8,1	7,3	0,3	6,7	8,5	5,1	9,9	22,4	23,5	-1,1	23,0	2,4
166	8,1	8,3	0,7	7,2	3,1	6,1	14,8	24,3	24,0	+0,3	24,2	0,6

B4. MODIFIED METHODS USED DURING THE ORIENTATION SURVEY OF BOREHOLE WATERS

B4.1 Mercury

This remained essentially the same as the cold vapour method of Hatch and Ott /22/ but a newer and more sophisticated mercury analyzer was used. It was designed by the NPRU/CSIR in Pretoria and was kindly loaned by Dr. P. Butler and Dr. M. J. Orren. In this analyzer the water vapour that tends to interfere with the AA signal is removed by anhydrous magnesium perchlorate. Mercury standards were periodically injected into the real sample matrix with a micropipette to test for matrix effects, but these were negligible. The analyzer was used in conjunction with a Varian Techtron AA6 in the "Absorbance Damp B" mode. The detection limit was 10 ng/l, with no known serious interferences at these levels. During the study of the Tsumeb mine waters (B3.) mercury solutions were preserved with perchloric acid, but the borehole waters were preserved with nitric acid. This did not appear to have any effect on the determination of mercury.

B4.2 Modified methods for the determination of certain heavy metals

Better methods of analysis for heavy metals were adopted as the project progressed, and solvent extraction procedures were used extensively for preconcentrating many metals. The methods developed by the writer during the orientation study of borehole waters are described in B4.2.1. Many of the analyses required in ancillary studies, such as those described in Appendix J, were kindly performed by the Assay Department of TCL. The methods used by TCL did not differ in any important aspects from those recorded elsewhere in this appendix.

B4.2.1 DETERMINATION OF *Cr, Mn, Fe, Co, Ni, Cu, Au, Zn, Cd, & Pb* IN BOREHOLE WATER

(a) Discussion

These metals were determined with the carbon rod (VT 63/AA6) after preconcentration. Nine of the elements were extracted with MIBK/APCD at pH3 and manganese was preconcentrated in a second step using MIBK/APCD and oxine at pH>7. This was necessary because manganese could not be extracted successful at pH3 with APCD alone, while oxine interfered with determination of some of the other elements.

Detection limits of less than 100ng/l were achieved for most of the metals examined. This was taken as a convenient value for the lowest standard and no attempt was made to interpolate between this standard and

the blank value; there was nothing to suggest that accurate determinations of concentrations of less than 100 ng/l would have been of any practical value in geochemical exploration in the Otavi Mountainland.

Stringent precautions were exercised against contamination /158,164-5, 169,28/. Some problems were encountered with lead and this was almost certainly due to aerosol Pb from automobile exhausts. The problem was minimized by working late at night when few automobiles were present and by wearing overclothing to reduce the emanation of aerosol particles from clothing and hair.

Interference tests were conducted by spiking an artificial borehole water with each of the metals studied. This water contained significant amounts of Ca, Mg, Na, K, chloride, sulphate, fluoride, phosphate and nitric acid and traces of most of the heavy metals. Table B4.2A provides an example of the kind of data collected during these tests. For each of the metals studied the recoveries obtained were acceptably similar to those obtained from pure water. The work of Orren and Corrigan (unpublished, 1973) provides additional reason for having confidence in the quality of the data produced by the methods described here. They analyzed certain international standard water samples by methods essentially identical to those used by the writer, and in the same laboratory. Their results are shown in Table B4.2B.

(b) *Apparatus and reagent*

250 ml Pyrex glass graduated measuring cylinders with plastic stoppers

Magnetic stirrer and Teflon-coated followers

pH meter and glass electrode

HNO₃ AR May and Baker

NH₄OH AR BDH number 10011

APCD BDH number 13008

Oxine AR BDH number 10131

MIBK AR Merck Art. 6146

Standard solns. 1000 mg/l BDH or Hopkins & Williams

Teepol for cleaning glassware

Varian Techtron AA6 spectrophotometer with Model 64 carbon rod analyzer

Micropipette (5µl) with disposable polyethylene tips

(c) *Procedure*

Place 250 ml of sample in a covered 400 ml beaker containing a magnetic follower. The beaker is placed on a stirring plate and the pH electrode

TABLE B4.2A

EXAMPLE OF DATA OBTAINED DURING EXAMINATION OF INTERFERENCES IN AAS ANALYSIS

Absorption values for Cu in distilled water and artificial borehole water

	1	2	3	4	1h	2h	3h	4h
blank	001	000	008	009	000	000	000	000
blank	002	000	011	009				
0,1 µg/l	160	157	160	175	003	003	003	002
0,1 µg/l	162	158	158	177				
1,0 µg/l	1299	1321	1360	1349	016	016	018	017
1,0 µg/l	1292	1329	1344	1351				
10 µg/l	2366	2409	2427	2412	038	039	039	039

1. distilled water

2. distilled water, duplicate

3. artificial borehole water

4. artificial borehole water, duplicate

1h to 4h. corresponding non-atomic signals with hydrogen lamp

NOTE: The slight signal produced by blanks 3 & 4 are almost certainly due to traces of copper in the reagents used to concoct the artificial borehole waters.

TABLE B4.2B

ANALYSES OF INTERNATIONAL STANDARD WATER SAMPLES AT UCT IN 1973

(A) International Atomic Energy Agency standard W3

	accepted value	Orren and Corrigan
Cadmium	6,15	6,7
Lead	305	310
Copper	14,6	not detected
Zinc	9,88	not detected

(B) International Association of Geochemistry & Cosmochemistry std. W3

	accepted value	Orren and Corrigan
Cadmium	3,43; $\delta=0,42$	4
Lead	16 \pm 0,2	16
Copper	137 \pm 7	139
Zinc	190 \pm 7	190

All values are in micrograms per litre.

inserted. With stirring, adjust the pH to $3 \pm 0,1$ (assuming the samples are acidified) with NH_4OH . Use conc. ammonia at first and add a 5% soln. dropwise as the correct pH value is approached. Transfer to a measuring cylinder. Add 2 ml of a 1% w/v soln. of APCD, which must be prepared daily. Shake. Allow to stand for a few minutes while the complexes form. 20 ml MIBK and shake vigorously for 2 minutes. Allow the phases to separate. Standards and blanks are treated similarly and must have the same amount of preservative acid as the samples. With due regard for the stability of the extracted complexes and the decontamination procedures for the carbon rod, the following order of analysis is recommended: Cu, Pb, Au, Zn, Cd, Co, Ni, Cr, Fe. The determinations are made with the standard carbon rod techniques /24-8/. The operating parameters for the rod that the writer found to be most suitable are summarized in Table B4.2C.

After completion of these operations, raise the pH of the contents of the measuring cylinder to between pH 8 and pH 10. (It is assumed that a negligible volume of MIBK was used in the first analytical run). Add 2 ml of a 1% w/v solution of oxine in MIBK (prepared daily) and shake vigorously for 2 minutes. Allow the phases to separate. Determine the concentration of manganese in a manner similar to that described for the other heavy metals.

B4.2.2 ANALYTICAL METHODS USED BY THE ASSAY DEPT., TCL, FOR CERTAIN ANCILLARY ORIENTATION EXPERIMENTS DESCRIBED IN APPENDIX J

The methods used by TCL are not essentially different to those already described in this appendix. The methods for sodium, potassium, hardness, TDS etc. are recorded in subsection B3. The method for the determination of the heavy metals was very similar to that described in the foregoing subsection 4.2.1. The only modification of any significance was the use of bromophenol blue, rather than a pH meter, to indicate when the desired pH values had been reached.

B4.3 Modified method for the determination of Al and Ag in borehole water

Silver and aluminium were determined by AAS after a preconcentration step very similar to that described in subsection B4.2.1. The pH of the sample is adjusted to 6,0 with ammonia and the metals are extracted with MIBK and oxine. It is in fact quite feasible to determine Al and Ag in the same run in which manganese is analyzed (*vide supra*) but there are no cogent reasons for including these metals in that series of analyses; on the contrary, there are several reasons for not doing so: the run described

TABLE B4.2C

PARAMETERS FOR CARBON ROD OPERATION IN THE AAS DETERMINATION OF SOME METALS
EXTRACTED INTO MIBK

Drying stage:

$8\frac{1}{2} \pm \frac{1}{2}$ volt, 14 ± 4 seconds, depending on the age of the carbon rod

Ashing stage:

8 volt, 3 seconds

Atomization stage:

Element	Voltage	Time (sec.)
Cu	$8\frac{1}{2}$	$3\frac{1}{2}$
Pb	7	3
Au	$7\frac{1}{2}$	3
Zn	$6\frac{1}{2}$	$2\frac{1}{2}$
Cd	7	$2\frac{1}{2}$
Fe	$8\frac{1}{2}$	5
Co	$8\frac{1}{2}$	$3\frac{1}{2}$
Ni	$8\frac{1}{2}$	$3\frac{1}{2}$
Cr	$8\frac{1}{2}$	$3\frac{1}{2}$
Mn	8	$2\frac{1}{2}$

In the case of the more refractory metals Fe, Co, Ni and Cr it is necessary to decontaminate the rod at high voltage between samples.

in subsection B4.2.1 is very long and the complexes of Al and Ag are not very stable. Furthermore, the extraction of silver with oxine is much more specific if APCD is absent. In addition, the determination of aluminium is subject to significant interference from silicon. In order to obtain usable results the extraction process must be completed very rapidly and the separated MIBK stored in plastic. The addition of relatively small amounts of silicon dissolved from glass containers causes a marked suppression of the aluminium signal. This interference is much less severe in flame AAS and for this reason all those samples with more than 25 μg Al per litre were analyzed by the conventional method rather than by flameless atomization.

By spiking a natural sample containing less than 1 mg/l of silicon with additional amounts of the element up to 25 mg/l, the writer found that the aluminium signal at concentrations less than 25 μg /l could be depressed by up to 40%. Many of the low aluminium values reported in Chapter 3 are therefore probably too low. Since an examination of these results showed that aluminium was of very little interest as a pathfinder, it was considered unnecessary to improve the quality of the data.

No interference problems were encountered in the analysis of silver if oxine alone was used as the complexing agent.

The optimum settings for the carbon rod atomizer were:

Drying stage, both elements : $8\frac{1}{2} \pm \frac{1}{2}$ volts 14 ± 4 seconds, depending on the age of the rod

Ashing stage, both elements : 8 volts, 3 seconds

Atomization stage: Al 9 volts, 5 seconds ; Ag $6\frac{1}{2}$ volts, $2\frac{1}{2}$ seconds.

Aluminium is highly refractory and decontaminating the rod is difficult.

B4.4 Determination of As, Ge, Se and Te in borehole waters

(a) *Introduction*

These four elements were determined by a special AAS technique. The dissolved element is reduced to the gaseous hydride by the action of sodium borohydride and the gaseous reagents are introduced into a nitrogen-entrained hydrogen flame. The spectrophotometer used was a Varian Techtron AA6 and the apparatus used for the hydride reduction was a slightly modified version of the VT Model 64 Vapour Generation Kit. The principles of the method have been recorded in several papers /168,170-4/.

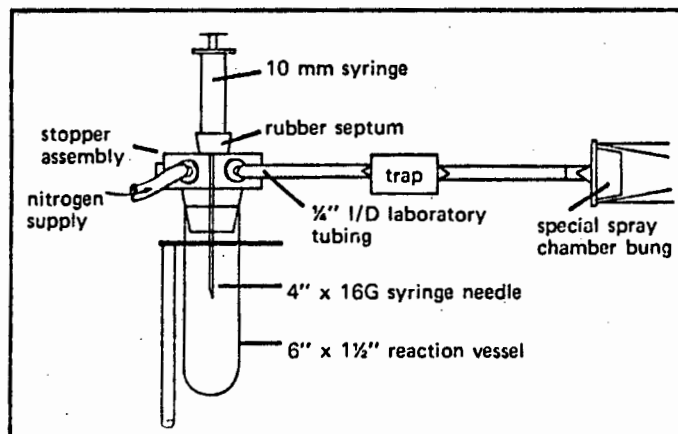
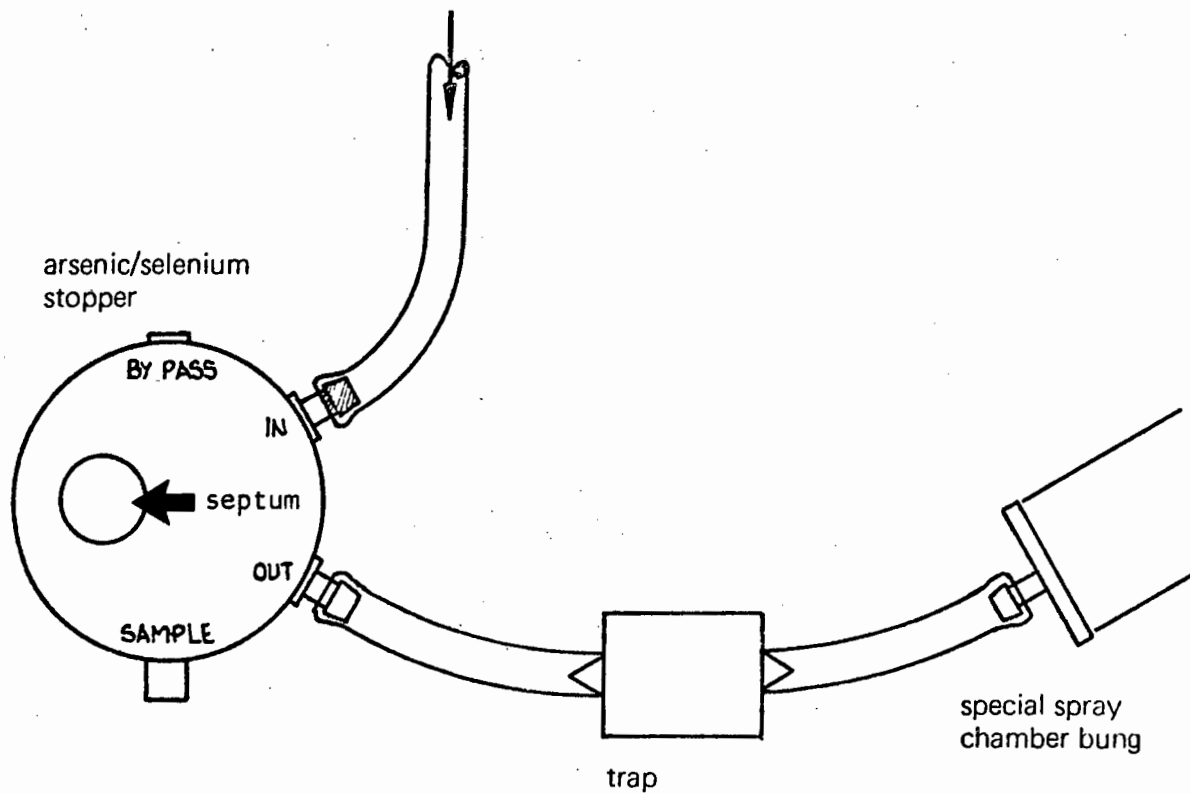


FIGURE B4. Apparatus for the generation of hydrides.

unstable. The writer's observations confirm those of Fernandez; the solid pellets are much easier to handle and convenient to use.

The installation and operation of the kit are well described in the VT AA6 handbook /174/ and in the abovementioned references but the following important points are not covered fully:

(i) Fernandez's claim /168/ to the contrary notwithstanding, the sample must be agitated during the reaction with the borohydride. This is achieved with the magnetic stirrer, which should be set at a speed that is fast enough to create a strong vortex almost to the bottom of the generator tube.

(ii) It is well known that oxidizing agents interfere with the formation of hydrides /172/. The samples from the boreholes were all preserved with nitric acid. This caused a deterioration of the detection limit but not of the precision of determination and the nitrate does not present a serious problem as long as the samples and standards are carefully matched with respect to the amount of nitric acid present. The loss of sensitivity due to the presence of nitric acid is not of great consequence in this project. Table B4.4A compares the detection limits reported by two other publications with those achieved by the writer in samples containing 20 ml of nitric acid per 800 ml of sample. The depression of the detection limit because of the nitrate is not more than 1 $\mu\text{g/l}$ for Se, Te and As and only 4 $\mu\text{g/l}$ for germanium.

The only other interference reported by the abovementioned authors is the suppression of the formation of tellurium hydride by gold and silver ions. However, these two metals are effectively absent from the borehole waters examined (Chapter 5). Guimont *et al.* (1977 /1181/) undertook a comprehensive study of the interferences that may be encountered in the determination of the elements of Groups VA and VIA by the borohydride method. The only significant interference is from nickel at concentrations of about 25 mg/l - a value vastly in excess of any concentrations of nickel encountered in the natural waters of the Otavi Mountainland.

(iii) There is little difference between the results obtained using the H_2/N_2 flame and those obtained with the H_2/Ar flame. The nitrogen entrained flame may even be a little better for As and Te because it absorbs less light at shorter wavelengths than Ar does. Nitrogen is much the cheaper gas.

There is little difference in performance between the air/propane and air/acetylene burners (Varian). The latter is preferred, as it is less prone to flashback.

(iv) The nitrogen entrained hydrogen flame is very "soft" and in order to obtain good results it must be very well protected against draughts.

TABLE B4.4A

REPORTED DETECTION LIMITS FOR THE AAS DETERMINATION OF As, Se, Te AND Ge

	Duncan and Parker /171/	Fernandez /168/	This work
Ge	2,0	10	6,0
As	0,1	0,5	0,6
Se	0,2	0,25	0,8
Te	0,35	0,25	0,9

All values in $\mu\text{g/l}$ *DETAILS:*

Duncan and Parker: Sample volume 20 ml; hollow cathode lamp; nitrate free.

Fernandez: Sample volume 20 ml; hollow cathode lamp; nitrate free.

This work: Sample volume 25 ml; hollow cathode lamp; 20 ml conc. nitric acid per 800 ml sample.

(v) The narrow orifices in the slip valve of the stopper tend to become blocked after a while by borate crystals thrown up in a fine spray by the effervescing pellets. This reduces the sensitivity of the AAS signal. The stopper must be regularly rinsed in distilled water.

(vi) The forms in which the elements studied are most likely to be present in natural waters are as follows: As(III), Se(IV), Ge(IV) and Te(IV) /35/. The standards used *must* be in the same oxidation state. This is critically important for tellurium; the reduction of Te(VI) by borohydride is very slow and erratic.

(vii) Various other information that will be of use to those who wish to perform this type of analysis with the VT AA6 is summarized in Table B4.4B.

Once the instrument has been set up and optimized /168,171,174/ the following procedure is followed: Light the flame. Select peak mode. To a clean generator tube containing a magnetic follower add 25 ml of sample by pipette. Add the appropriate aliquot of acid from the autodispenser (Table B4.4B). Clamp the tube in position on the stirrer plate and firmly insert the stopper valve, which should be in the "sample" position. In the case of Se and As the absorption indicator needle on the spectrophotometer will oscillate slowly and then settle down after a few seconds as nitrogen from the support supply fills the generation tube and the line to the nebulizer. Remove the glass stopper from the Tygon tube attached to the septum orifice of the stopper. Constrict the tube near the bottom with the fingers and drop a pellet of borohydride into the tube with the plastic forceps. Replace the glass stopper firmly into the Tygon tube and start the stirrer. Press the zero button for about three seconds. Release the pressure on the Tygon tube so that the pellet falls into the sample. A very vigorous reaction will occur. In the case of As, Te and Se, press the "read" button on the spectrophotometer immediately. In the case of Ge wait about one second before activating the read process. If there is any doubt about the rate at which the the AA signal builds up, run a few test samples and watch the development of the peak on the absorption indicator needle. Run a distilled water blank and standards. The writer found that blank values were negligible and that there was no interference from non-atomic absorption. The best way of preparing standards is by the method of additions /28/, i.e. by using a micropipette to inject known, small masses of the analyte directly into aliquots of the sample being analyzed. This reduces matrix effects to a minimum.

B4.5 Measurements of redox potential in borehole waters

TABLE B4.4B

GAS PRESSURE SETTING FOR THE VT AA6 AND ACID CONCENTRATIONS FOR SAMPLES
IN THE DETERMINATION OF As, Se, Te AND Ge BY HYDRIDE REDUCTION

(1) *Primary settings for cylinder regulators*

For all elements: Hydrogen 25 psi Nitrogen 40 psi

(2) *Consumption of gas*

One element in 50 samples takes four hours and uses $\frac{3}{4}$ of a 2100 lb H₂ cylinder containing 206 ft.³ at STP, and one quarter of a similar cylinder of high purity dry nitrogen.

(3) *Secondary pressures and acidification of samples*

ELEMENT	ACID PER 25 ML SAMPLE	N ₂ FLOW GAUGE	H ₂ SETTINGS
Se	25 ml conc. HCl	2,5	5,0
As	20 ml conc. HCl	7,8	4,5
Te	20 ml conc. HCl	5,0	5,0
Ge	10 ml conc. H ₂ SO ₄	4,0	4,0

Notes:

Te: The sensitivity of determination is not greatly influenced by the secondary pressure settings.

Ge: Set the height of the burner to 10 for germanium determinations. The mixture of sample and H₂SO₄ must be cooled before analysis.

Measurements of the redox potential of groundwaters are recorded in Appendix J. It is important to note that these values are simple millivolt readings with respect to the electrodes employed. At first sight the measurement of the redox potential is straightforward and has been adequately described by Truesdell /1189/ and others /982,1190/. A suitable reference electrode is inserted into the solution and the potential that develops is taken as a measure of the tendency towards oxidation or reduction of given substances in that solution. However, very serious practical problems are involved in the accurate measurement and interpretation of Eh values in groundwaters /1189-90/; the difficulties posed by oxygen contamination and mixed potentials are examples. For this reason, no attempt has been made to derive sophisticated Eh data from the experimental readings recorded in Appendix J. The object has been simply to detect any gross relative changes in the redox potential of various groundwaters and, in particular, to identify any highly reduced waters with strongly negative mV values.

B4.6 Determination of Cu, Pb and Zn in TSS residues

In part B3 of this appendix methods were described for (a) the determination of the concentration of total suspended solids (TSS) in groundwaters, and (b) the semi-quantitative examination of the composition of these TSS residues by XRFs.

It was necessary, for the purposes of the orientation experiments described in Appendix J, to obtain much more precise data for the concentrations of copper, lead and zinc in the TSS residues of certain samples of borehole waters. These data were obtained by weighing and dissolving the Millipore discs containing the residues and analyzing the resultant solution by AAS. The disc was placed in a clean, dry, 8 inch test tube and 2 ml of concentrated nitric acid was added. The tube was heated for 10 minutes. The disc dissolved completely and in all cases at least 90% of the material upon it also went into solution. The remainder was mainly silica and clay and therefore of little interest anyway. Blanks, consisting of new, clean discs, were treated similarly. The solutions in the test tubes were made up to 10 millilitres. The AAS methods of analysis used were in all essential details analogous to those described in subsection B3. Numerous checks were made to ensure that the data obtained were precise and that the presence of the products of decomposition of the cellulose discs did not have an adverse effect on the quality of the results. Table B4.6 shows data obtained from a series of duplicate blanks and copper standards made up either in pure water or in a solution of a millipore disc.

TABLE B4.6

EXAMINATION OF NON-ATOMIC ABSORPTION AND MATRIX EFFECTS IN THE AAS ANALYSIS
OF Cu IN TSS RESIDUES

	1	2	3	4	1h	3h
blank	001	002	008	011	000	000
blank	000	000	009	009	000	000
0,1 mg/l	160	162	160	158	003	003
0,1 "	157	158	175	177	003	003
1,0 "	1299	1292	1360	1344	016	018
1,0 "	1321	1329	1349	1351	016	017
10 "	2366	2380	2427	-	038	039
10 "	2409	-	2412	2440	039	039

1 & 2: Duplicate sample-readings - no cellulose

3 & 4: Duplicate sample readings - with cellulose

1h & 3h: Corresponding non-atomic signals

It can be seen that the non-atomic absorption signal is less than 5% of the total signal. The presence of the products of dissolution of cellulose appears to cause an enhancement of the copper signal by only about 5%. Both of these effects can be ignored for the purposes for which the data were required. In the cases of zinc and lead the non-atomic and interference errors were of the order of only 1-2%.

B4.7 Modified method for sulphate

It proved to be convenient to replace the scintered glass disc used for trapping the precipitated sulphate (subsection B3.4) with a Millipore disc. Since sulphate is an important potential pathfinder, it was deemed necessary to check the acceptability of this change with recovery and precision tests, which are documented in Table B4.7.

B4.8 Modified methods for XRFS analysis of TSS residues

The methods used for Ca, Ti, Mn, Fe, Cu, Pb and Zn were very similar to those described in Table B3.8 but the flow counter was not used. A semi-quantitative method for Mg, P, Al and Si, which gave better results, was adopted and the relevant instrumental parameters are compiled in Table B4.8.

B4.9 General observations on the quality of the data for the major components of the borehole orientation samples

(A) *Precision of multiple analyses*

Data for multiple analyses of Na, K, Ca, Mg, sulphate, chloride and fluoride are compiled in Tables B4.9(1) to B4.9(7). The quality of the data is quite adequate.

(B) *Ionic balances*

Ionic balances for the borehole orientation samples are compiled in Table B4.9(8). The imbalance between the anionic and cationic totals is given as a percentage of the total ionic concentration in milliequivalents (cf. subsection B3.). Of the 54 totals, 41 agree within 3%, 51 agree within 5% and only two are in error by more than 5½%. Exhaustive tests on the acidified reserve samples (Appendix G) showed that the larger errors (>4%) must in all cases have been due to difficulties encountered in the determination of bicarbonate. This corresponds to a maximum relative error

TABLE B4.7

RECOVERY AND PRECISION TESTS IN THE GRAVIMETRIC DETERMINATION OF SULPHATE

(1) *Recovery test*

Sample: Anhydrous AR sodium sulphate in pure water

Filter apparatus: Millipore vacuum filtration system; 47 mm discs; RAWP 047 00 AA cellulose filters, 0,8 μm pore size.

	Mass Na_2SO_4	Weighed BaSO_4	Required BaSO_4	Recovery %
1	0,1337 g	0,2219	0,2197	101,0
2	0,1984	0,3289	0,3260	100,9
3	0,4035	0,6703	0,6630	101,1
mean mass of blank: minus 0,0002 g				

(2) *Precision tests*

SAMPLE A: TSUMEB TAP WATER

Four analyses, mg/l : 443 439 445 445

SAMPLE B: RAW MINE WATER

Ten analyses: 473 476 471 481 478 481 487 483 478 480
 mean = 478,8 $\sigma = 4,7$ $\% \sigma = 0,98$

TABLE B4.8

INSTRUMENTAL CONDITIONS FOR SEMI-QUANTITATIVE XRF'S DETERMINATION OF
Mg, P, Al AND Si IN TSS RESIDUES

Target : Cr 55KV, 36mA
 Vacuum : on
 Collimator : Coarse, 550 μ m
 Counter : Flow EHT = 551
 Counting time : 20 seconds on peak, 20 seconds on background
 Comparative standard used was G-2 (1968) /77/

	P	Si	Al	Mg
crystal	PET	PET	PET	ADP
pulse height A	390/260/1	EXT	EXT	EXT
Peak angle	89,20	108,80	144,80	136,58
Background ang.	88,20	106,5	140,0	132,0

TABLE B4.9(1)

MULTIPLE ANALYSES OF ORIENTATION SAMPLES FROM BOREHOLES

Sodium, mg/l

Sample	1	2	3
271	11,3		10
272	179	180	
273	5,1	4	5
274	5,0	4	5
275	4,1	3	4
276	33,0		33
277	6,2	5	6
280	3,3	3	3
285	20,8	16	20
288	63,0		56
297	16,2	14	16
299	85,0		78
301	45,1		44
302	4,5	3	4
305	0,9	1	1
306	1,0	1	1
319	2,2	2	2
321	2,3	3	2

All samples collected during the original borehole orientation, March 1974

TABLE B4.9(2)

MULTIPLE ANALYSES OF ORIENTATION SAMPLES FROM BOREHOLES

Potassium, mg/l

Sample	1	2
271	0,9	0,9
272	0,9	1,0
273	0,8	0,9
274	0,8	0,9
275	0,9	0,9
276	0,8	0,9
277	0,9	0,9
280	0,9	0,9
285	1,2	1,3
288	1,0	1,0
297	0,9	1,0
299	0,5	0,5
301	0,5	0,6
302	0,2	0,2
305	0,3	0,4
306	0,5	0,5
319	0,7	0,7
321	0,3	0,3

All samples collected during the original borehole orientation, March 1974

TABLE B4.9(3)

MULTIPLE ANALYSES OF ORIENTATION SAMPLES FROM BOREHOLES

Calcium, mg/l

Sample	1	2	3	4	5	6
271	108		108	108	104	
272	54	50	58	58	57	
273			92	92	94	
274			90	90	92	
275			96	96	95	
276			140	140	143	
277			108	108	112	
280			108	108	104	
285			104	104	108	
288			126	136	129	
297			114	114	124	112
299			198	198	189	
301			50	51	53	48
302			64	64	81	
305			84	96	82	
306			82	82	87	
319			90	90	89	
321			90	90	89	

All samples collected during the original borehole orientation, March 1974

Analysis number 5 by AAS; other analyses are titrimetric

TABLE B4.9(4)

MULTIPLE ANALYSES OF ORIENTATION SAMPLES FROM BOREHOLES

Sample	<i>Magnesium, mg/l</i>					
	1	2	3	4	5	6
271	64		64	64	65	
272	90	92	87	87	96	
273	45	49	56	56	54	
274	45	47		58	55	
275			57	57	58	
276			55	55	49	
277			53	53	53	
280			51	51	50	
285			83	83	80	
288			90	89	91	
297			97	97	93	105
299			149	149	147	
301			36	36	36	41
302	18	17	24	24	23	
305			52	52	50	
306			51	51	48	
319			49	49	50	
321	50	49	53	53	50	

All samples collected during the original orientation, March 1974

Analysis number 5 by AAS; other analyses are titrimetric

TABLE B4.9(5)

MULTIPLE ANALYSES OF ORIENTATION SAMPLES FROM BOREHOLES

Chloride, mg/l

Sample	1	2	3	4
271	45	45	58	
272	107	107	127	
273	8	8	15	
274	11	11	15	
275	10	10		
276			30	40
277	12	12		3
280	11	11		3
285	23	23	39	30
288			127	109
297			30	36
299			370	346
301	11	11		
302	8	8	15	
305	11	11	21	
306			24	30
319			15	24
321			24	30

All samples collected during the original orientation, March 1974.

TABLE B4.9(6)

MULTIPLE ANALYSES OF ORIENTATION SAMPLES FROM BOREHOLES

Sample	<i>Sulphate, mg/l</i>					
	1	2	3	4	5	6
271			46		37	42
272			312		293	341
273			11		15	
274			13	9		<20
275			9		3	
276		198	224			201
277		14	13			<20
280		16	15	12		<20
285		53	48			56
288		159	158			182
297		4	9			<20
299	50	79		45		67
301	22				18	20
302	<0,4	9			3	<20
305	<0,4	5	9		4	
306	<0,4	7			5	<20
319	6	10	11		1	<20
321	<0,4	6	6	1	2	<20

All samples collected during the original borehole orientation, March 1974

Analysis number 6 by AAS, residual Ba^{++} method /28/; other analyses are gravimetric

TABLE B4.9(7)

MULTIPLE ANALYSES OF ORIENTATION SAMPLES FROM BOREHOLES

Fluoride, mg/l

Sample	1	2
271	0,16	0,16
272	0,25	0,36
273	0,15	0,11
275	0,11	0,10
276	0,20	0,25
280	0,18	0,25
288	0,17	0,20
297	0,21	0,19
299	0,29	0,35
301	0,18	0,11
305	0,10	0,04
306	0,07	0,04

All samples collected during the original borehole orientation, March 1974

TABLE B4.9(8)

IONIC BALANCES FOR THE BOREHOLE ORIENTATION SAMPLES

<i>Sample number</i>	<i>cations meq.</i>	<i>anions meq.</i>	<i>diff. %</i>
271	11,44	12,53	4,91
272	18,87	19,75	2,28
273	9,67	10,27	3,01
274	9,48	10,46	4,91
275	9,93	10,21	1,39
276	12,76	13,97	4,53
277	10,28	12,64	10,30
278	10,47	10,65	0,85
279	11,09	10,88	0,96
280	9,90	15,43	21,82
281	9,98	9,88	0,50
282	10,70	10,88	0,83
283	10,21	10,44	1,11
284	10,68	11,18	2,29
285	12,99	13,13	0,54
286	10,81	10,34	2,22
287	10,31	10,52	1,10
288	17,05	16,42	1,88
289	10,35	10,60	1,19
290	10,70	10,16	2,59
291	9,75	9,82	0,30
292	11,14	10,77	1,69
293	11,78	11,16	2,70
294	9,10	9,21	0,60
295	11,24	11,47	1,01
296	13,73	13,63	0,37
297	14,39	13,12	4,61
298	12,21	12,45	0,97
299	26,23	24,11	4,21
300	11,88	12,23	1,45
301	7,53	7,95	2,71
302	5,42	5,73	2,78
303	13,64	14,15	1,83
304	10,50	10,65	0,71
305	8,56	9,18	3,49
306	8,29	9,24	5,42
307	65,47	65,55	0,06
308	8,09	8,61	3,11
309	9,47	9,62	0,79
310	12,09	12,59	2,03
311	13,82	13,60	0,86
312	6,76	7,01	1,81
313	9,82	10,35	2,63
314	8,05	8,40	2,13
315	8,76	8,87	0,62
316	6,20	6,13	0,57
317	10,01	10,39	1,86
318	16,91	17,60	2,00
319	8,94	9,24	1,65
320	10,00	9,98	0,10
321	8,93	9,66	3,92
322	9,13	9,35	1,19
323	9,68	9,75	0,36
324	9,08	9,77	3,66

of 30% in the determination of this ion. Because the reserve sample had been acidified it was not possible to check the concentration of bicarbonate directly. The occurrence of significant errors in one or two of the bicarbonate determinations is hardly serious, since this ion later proved to be of meagre importance as a hydrogeochemical pathfinder (Section 3).

B5. ANALYTICAL PROCEDURES FOLLOWED DURING THE APPLICATION PHASE

B5.1 GENERAL

The following were measured or determined in the samples from the Withdrawal area: Ph, M alkalinity, P alkalinity, calcium hardness, total hardness, TDS, sulphate, chloride, sodium, copper, lead and zinc. The analytical methods used have all been described in subsections B3. or B4. and it is necessary to consider only some minor modifications that were made to the methods used to determine the last mentioned four metals.

(i) *Copper, lead and zinc*

Perchloric acid was substituted for nitric acid as the preserving acid and due allowance was made for this in the preparation of blanks and standards. No untoward effects were noticed. The volume of sample used was 200 ml and bromophenol blue (yellow to blue at pH 3) was used to indicate when the desired pH value had been reached. Twenty mls. of MIBK were added. A chart recorder was used to measure the heights of the peaks. A wide range of samples was checked for the presence of non-atomic absorption signals but this was negligible in all cases. No attempt was made to detect concentrations of metals below 1 µg/l because the orientation study had shown that this was unnecessary.

(ii) *Sodium*

The aliquots used for the determination of sodium were not spiked with an alkali metal or lanthanum. The sodium data for the application study are thus not as accurate as those collected during the orientation survey, but are nevertheless quite adequate for the purpose of hydrogeochemical interpretation.

B5.2 CONTROL OF PRECISION AND RELATED TESTS

Many of the tests that were instituted to measure precision, monitor trace element contamination etc. have been described in foregoing

subsections. Only those additional tests that were not strictly part of the orientation experiment are discussed here. In order to retain some control over the precision of the routine analyses of the samples from the Withdrawal area, a check sample was submitted with each batch of determinations. Three classes of check samples were used - one for wet chemical analyses of major components, one for Cu-Pb and one for Na-Zn. The results obtained from these three checking systems are discussed below.

(1) Check samples submitted for wet chemical analysis

Twenty one undeclared samples were submitted for analysis twice. The results are compiled in Table B5.2(1). The precision obtained is of the same order as the precision for the analysis of the borehole orientation samples (subsection B4.9) and are quite adequate for the purposes of hydrogeochemical interpretation and the identification of anomalies.

(2) Check samples analyzed for copper and lead

Results of the reanalysis of undeclared samples are compiled in Table B5.2(2). They are typical of routine trace element determinations at very low levels relatively near to the detection limit. The reproducibility is good enough to allow the ready identification of the few values that rise significantly above the general background.

(3) Check samples analyzed for sodium and zinc

Results of the reanalysis of undeclared samples are compiled in Table B5.2(3). Compared to copper and lead the relative precision is greatly improved, because the concentrations of zinc and sodium are generally well above the respective detection limits for these two metals. Anomalous analyses are reproducible and can be unambiguously identified.

TABLE B5.2(1)
 DUPLICATE ANALYSES OF MAJOR COMPONENTS IN CHECK SAMPLES COLLECTED FROM
 BOREHOLES IN THE WITHDRAWAL AREA

sample	pH	CaH	MgH	TH	TDS	Cl ⁻	PA	MA	SO ₄ ⁼
1	6,8	240	314	560	584	49	nil	565	5
	6,8	252	308	560	604	49	nil	565	-
2	6,8	200	356	556	604	36	nil	555	4
	6,8	200	356	556	608	36	nil	555	-
3	6,8	68	508	576	648	36	nil	590	7
	6,75	68	508	576	648	36	nil	590	-
4	7,0	88	440	528	604	36	nil	500	9
	7,0	88	440	528	592	49	nil	500	-
5	6,9	112	380	492	560	36	nil	490	9
	6,9	112	380	492	544	36	nil	490	-
6	6,8	100	444	548	776	24	nil	455	111
	6,9	100	444	548	760	24	nil	455	-
7	6,8	336	344	680	620	109	nil	495	20
	6,9	324	346	670	536	103	nil	490	17
10	6,8	464	566	1030	1292	306	nil	605	37
	-	-	-	-	1308	-	-	-	-
11	6,7	284	386	670	516	29	nil	690	10
	6,7	288	392	680	544	34	nil	690	9
17	7,10	208	152	360	448	6	nil	370	6
	7,00	208	152	360	428	7	nil	370	5
19	6,90	248	272	520	544	6	nil	540	10
	6,90	252	268	520	516	6	nil	540	10
26	6,8	312	338	650	796	44	nil	610	14
	7,0	312	348	660	800	41	nil	600	18
33	7,0	260	400	660	788	66	nil	550	9
	7,9	260	400	660	744	73	nil	540	5
52	7,2	-	-	-	-	-	-	-	-
	7,5	216	234	450	576	55	nil	395	11
59	7,4	216	234	450	560	55	nil	395	10
	7,9	304	836	1140	4796	936	nil	455	225
72	7,9	304	816	1120	4064	770	nil	455	185
	7,2	104	1376	1480	3396	885	nil	490	111
89	7,4	104	1376	1480	3572	885	nil	490	107
	7,2	280	330	610	1028	145	nil	430	35
96	7,2	312	428	740	1160	193	nil	445	41
	7,5	224	226	450	476	18	nil	470	5
106	7,5	224	226	450	460	18	nil	470	4
	7,2	148	412	560	1708	312	nil	640	409
110	7,3	144	416	560	1708	297	nil	640	418
	7,4	72	588	660	5044	441	nil	1730	1693
166	7,4	60	610	670	5052	441	nil	1730	1697
	7,0	316	494	810	1564	218	nil	525	88
	7,1	320	500	820	1576	218	nil	525	91

Calcium hardness, magnesium hardness, total hardness, phenolphthalein and methyl orange alkalinity all expressed as ppm calcium carbonate. Other analyses in mg/l. Sample numbers appear on Map 4a in Volume 2.

TABLE B5.2(2)

REANALYSIS OF SAMPLES OF BOREHOLE WATERS FOR COPPER AND LEAD

sample	1st Cu	2nd Cu	3rd Cu	1st Pb	2nd Pb	3rd Pb
6	3	4	4	7	<1	<1
13	<1	<1	-	4	<1	-
15	2	7	-	<1	3	-
16	<1	<1	-	11	7	-
17	2	5	-	6	3	-
18	<1	<1	-	2	2	-
22	5	13	-	4	3	-
23	56	44	-	2	2	-
31	4	5	-	6	6	-
37	4	5	-	<1	<1	-
55	6	2	-	4	3	-
56	22	25	10	<1	<1	1
63	6	4	-	<1	1	-
70	17	8	-	<1	5	-
74	1	<1	-	<1	<1	-
96	3	14	2	<1	<1	<1
100	<1	9	-	<1	<1	-
111	6	12	-	<1	<1	-
113	35	70	-	<1	<1	-
123	13	16	-	<1	<1	-
134	1	1	<1	<1	<1	<1
147	11	11	21	<1	<1	<1
158	14	13	10	<1	<1	<1
171	10	10	7	<1	<1	<1

All values are in micrograms per litre

All sample numbers appear on Map 4a (Withdrawal area) in Vol. 2

TABLE B5.2(3)

REANALYSIS OF SAMPLES OF BOREHOLE WATER FOR ZINC AND SODIUM

sample	1st Zn	2nd Zn	3rd Zn	1st Na	2nd Na	3rd Na
1	745	750	-	7	6	-
14	43	93	88	15	15	15
25	113	120	151	5	5	5
38	71	76	66	10	13	10
49	56	54	49	15	15	14
61	58	57	52	20	20	20
73	125	126	121	5	6	6
85	46	50	55	220	220	180
97	20	18	18	30	30	30
109	68	67	64	120	120	100
121	49	47	70	180	180	200
133	24	24	19	18	18	18
145	65	62	84	20	20	20
157	45	50	90	8	8	8
169	5	5	6	6	6	6
1204	21	21	-	0	0	-

Zinc in micrograms per litre, sodium in milligrams per litre.

All sample numbers except 1204 (a control sample) appear on Map 4a in Volume 2.

APPENDIX C

The construction of Figure 1 (Long section through the Tsumeb pipe) and the method of projection onto it of the locations of the sampling points of the thirty six orientation water samples from the mine

The reader is referred to Figures 1 and 1a and Maps 2 and 3 in Volume II. The principle features of Fig. 1 have been copied from a diagram entitled "Section showing the structural setting of Tsumeb ore body in stratigraphic sequence of the Tsumeb syncline (Revised N.C.T. 1971)". This diagram was produced by geologists at Tsumeb Corporation Limited (TCL) and is the corporation's standard, full-length, geological long section through the pipe. At the time that Fig. 1 was produced (June 1975) the only other modern geological long section diagram available was that of Hopwood /233/, but this was less suitable.

The standard long section has certain characteristics that should be noted: (1) The surface lithological contacts and topography are accurately represented. The geology of the pipe structure and the adjoining country rocks is also accurately drawn and is based on extensive underground mapping and diamond drilling. Further away the depicted geology becomes increasingly more schematic. The lithological features of the pipe in the plane of section are not necessarily typical of the entire structure at a given depth. (2) The standard long section is not one continuous plane, but is a composite of three slightly different, vertical, sectional planes projected onto the same sheet of paper. It is so constructed because no one vertical plane can adequately represent the pipe structure over its entire length. This fact is illustrated by Fig. C1a, which is a vertical long section through the pipe, at right angles to the section in Fig. 1. Although the pipe is essentially vertical, it is not quite straight. Zero section (underground co-ordinate eastings) is an ideal cross-section for depicting the geology of the middle levels, but it is not suitable for either the upper or the very deep levels where the location of the important ore is displaced to the west of the zero line.

The orientation of and the relationships between the three sectional subplanes that comprise Fig. 1 are shown in Map 2. The first plane, on 38 section, extends from surface to 20 level. Here the line of section swings through an azimuth of approximately ten degrees and thus, between 20 and 43 levels, the new plane of section is zero section. This swing should of course produce a slight dislocation in the Standard Section at 20 level, but this irregularity is smoothed out (Figs. C1b & c), so that the depicted

geology is continuous through 20 level. The effect of this smoothing is negligible. The standard section is again smoothed at 43 level, where the plane of section takes a parallel jump to W30 section. These changes in the plane of section also produce apparent dislocations in the vertical shafts; these can scarcely be smoothed out and De Wet shaft therefore appears to have a kink in it at 20 level. (3) The sampling points were plotted on Fig. 1a by normal projection onto whichever of the three vertical subplanes was relevant. This type of projection is shown in Fig. C1d. The long section cannot show how far behind or before the paper the represented sampling point lies. Therefore the sampling point is shown located relative to the geology of the standard section and *not* relative to its real geological setting. This approximation has to be accepted as a practical solution to the problem of representing scattered points within a geological solid. This shortcoming is lessened to some extent by the data provided in the miniature plan sections of each sampling point (Fig. 1a; cf. Appendix A). By using the two sets of orientation data in Fig. 1a the reader can construct a mental picture of the real location in space of the sampling point, and of the stereo-orientation of the boreholes shown.

The detailed procedure for projecting the sampling points onto Fig. 1a was as follows (Fig. C2):

- (1) All co-ordinates used were in the local underground system.
- (2) The co-ordinates of all sampling points were known from level survey plans (e.g., Map 2).
- (3) The co-ordinates of De Wet shaft (Map 2) are known. The co-ordinates of the point of projection of De Wet shaft onto each of the three vertical subplanes (*vide supra*) was measured on Map 2.
- (4) Let (x_1, y_1) be any such known point on the line of projection. i.e., the locus of the intersection of the vertical subplane and any given level plan. Let (xy) be the real co-ordinates of any sampling point. Then

$$c = y_1 - x_1 \tan (90-a)$$

and

$$X_1 = c / \tan (90-a) = (x_1 \cot a - y_1) / \cot a \quad \dots (i)$$

Furthermore,

$$n = X_1 - x$$

$$m = y \tan a$$

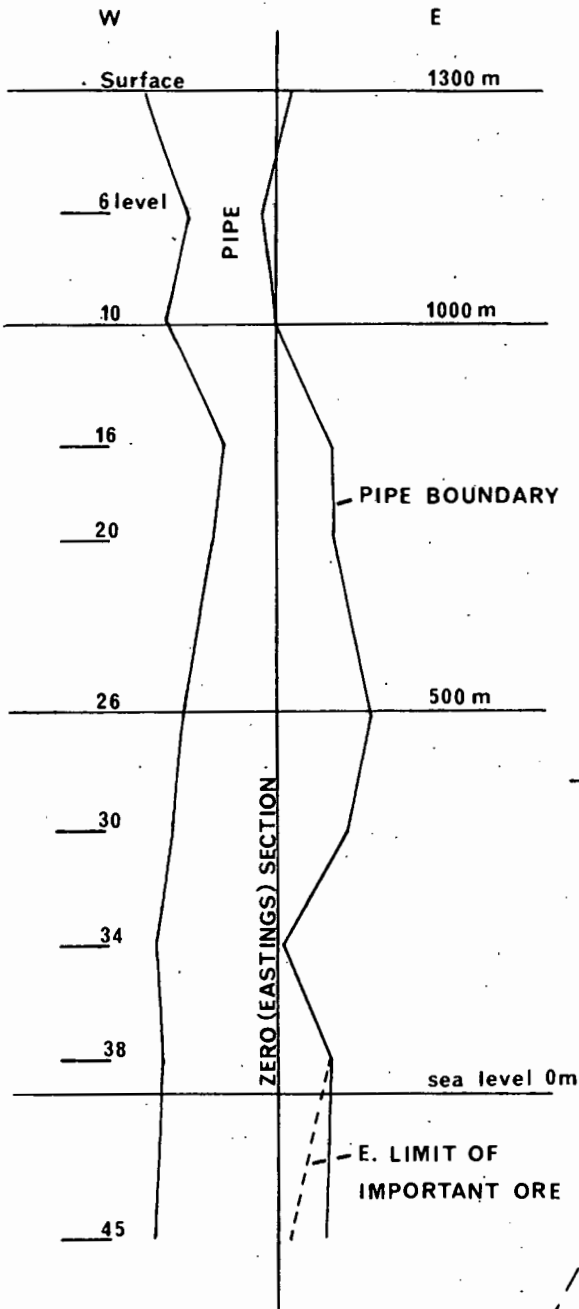
$$z = (m+n) \sin a$$

and

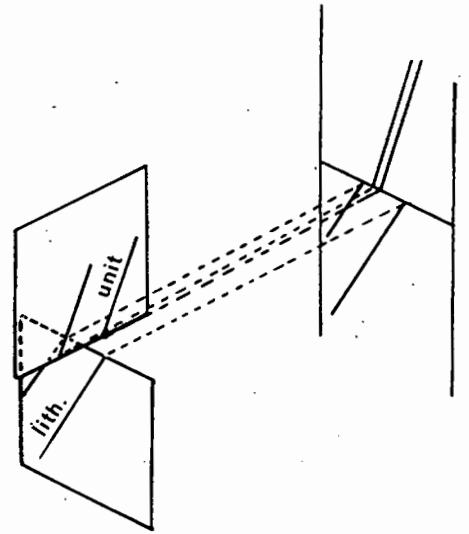
$$k+z = y / \cos a$$

FIG. C1

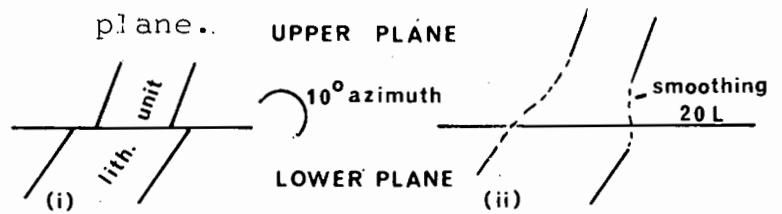
LONGITUDINAL (E-W) LONG SECTION THROUGH THE TSUMEB PIPE & DIAGRAMS ILLUSTRATING THE "SMOOTHING OUT" OF DISTORTIONS PRODUCED BY ROTATING THE PLANE OF SECTION IN FIG. I, VOL. II.



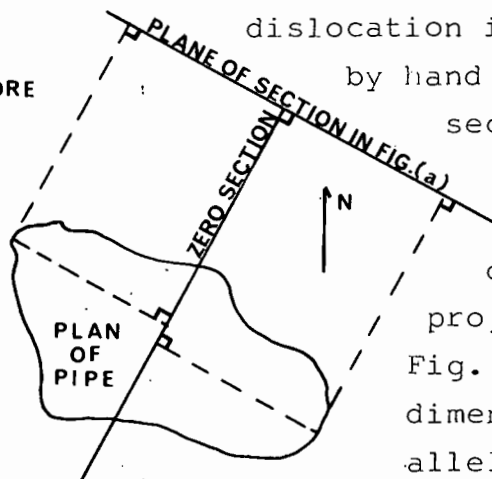
a. E-W long section through the Tsumeb Pipe. One continuous plane, shape measured at intervals of about 5 levels; projection shown in Fig. d, (above, right). See Text.



b. Exaggerated example of the apparent dislocation produced when part of the plane of section through a lithological unit is rotated and the new intersection projected onto the original plane.



c. (i) Schematic example of the dislocation described in (b), above; at 20 Level in Fig. I, Vol. II, due to rotation through about 10° of the plane of long section through the pipe. The dislocation is "smoothed out" by hand in the finished section. (ii)



d. Explanation of projection used in Fig. a, (left). Max. dimension of pipe, parallel to Zero (easting) Section, projected onto an arbitrary plane normal to that Section.

Therefore

$$\begin{aligned}
 k &= (y/\cos a) - z \\
 &= (y/\cos a) - (m+n) \sin a \\
 &= (y/\cos a) - (y \tan a + (X_1 - x)) \sin a \quad \dots(ii)
 \end{aligned}$$

If any (x_1, y_1) is known then X_1 can be calculated for any sectional plane of known azimuth a by using equation (i). By substituting X_1 in equation (ii), the arbitrary distance k can be calculated for any (xy) . Substitution of the real co-ordinates $(x'y')$ of De Wet shaft for (xy) gives k' . Since the position of (x_1, y_1) is known, any value k can be plotted relative to (x_1, y_1) as $(k'-k)$.

A Tektronix Scientist 909 desk calculator was programmed to calculate $(k'-k)$ in this manner for the thirty six sampling points. The key values measured or calculated are shown in Table C. The distances $(k'-k)$ were then plotted on Fig. 1a relative to the projected position of De Wet shaft at the required level, using the scale 1:5000.

TABLE C

PROJECTED LOCATIONS OF THE COLLECTION POINTS FOR MINE WATER SAMPLES

Sectional subplane	x_1	y_1	a	k'
0 to 20 level (38 Section)	1760	1932	10 ⁰	1786,0
20 to 43 level (Zero Section)	1696	1937	23,9 ⁰	1854,1
Below 44 level (W90 Section)	1709	1908	23,9 ⁰	1868,2

sample	$(k'-k)$	sample	$(k'-k)$	sample	$(k'-k)$
131	73,1	143	-12,8	155	77,6
132	91,8	144	80,0	156	162,9
133	108,0	145	-21,2	157	71,3
134	73,1	146	108,5	158	158,7
135	106,7	147	-14,6	159	73,1
136	-32,3	148	104,9	160	62,7
137	185,6	149	53,4	161	221,3
138	144,3	150	89,9	162	85,2
139	39,6	151	94,6	163	307,6
140	62,0	152	93,0	164	106,7
141	107,0	153	43,8	165	162,9
142	157,3	154	232,1	166	92,4

APPENDIX D

An alternative approach to the interpretation of the Tsumeb mine water data

The writer's interpretation of the meaning and significance of the data collected during the orientation study of the Tsumeb mine waters has been set out in detail in Chapter four. The principle features of this interpretation, or model, are as follows:

- (1) The interpretative model for the mine waters (the hydrogeochemical model) is based firmly on a primary hydrological model, which traces the origin and evolution of the various types of waters sampled. i.e., the significance of the composition of any sample is seen in terms of the previous history of that particular water - as far as it is known - as well as the present chemical state of that sample in its relationship to adjacent mineralization.
- (2) It is argued that only sodium, chloride and sulphate - being well concentrated and very mobile - can be meaningfully used to construct the primary hydrological model. i.e., these three ions are the only reliable natural tracers. The very low levels of concentration and the general relative immobility of the trace elements render them readily susceptible to fluctuations in abundance that are not related purely to dilution and mixing of waters. They cannot therefore be relied upon as natural tracers. The species calcium, magnesium and bicarbonate are also not reliable, because they are controlled by the carbonic system. In a dolomitic country rock the concentrations of these three ions in formational waters will be affected by factors such as pH and $p\text{CO}_2$, which have little influence on the concentrations of sodium, chloride or sulphate.
- (3) Thus, in the hydrological model, the samples are arranged in Groups and subgroups on the basis of the Na/Cl^- ratio and to some extent on the absolute concentrations of the three mobile ions and the depth below surface.
- (4) One of the implications of the model is that mine water is being recycled via the surface on a large scale (Appendix H).
- (5) This recycling has had a major effect on the chemical composition of the groundwaters presently associated with the mine workings. The writer believes that recirculation of this kind has very probably upset some of the natural chemical relationships and balances in these waters and that this severely restricts the confidence that can be placed in the usefulness of the mine water samples for purposes of orientation.

Viewing (pers. comm. 1975 and unpublished documents /283-5/), using *only the data from this thesis*, has adopted a radically different approach

to the interpretation thereof. By starting with fundamentally different initial assumptions he has arrived at conclusions that depart markedly from those of the writer.

Viewing's documentation is voluminous and largely informal and it is not possible to present more than a summary of his approach to the interpretation of the mine water data. The assumptions attributed to him include both those that are explicit and implicit but any error in this regard is entirely the writer's.

(1) Viewing's is a straight, empirical approach. There is little emphasis on hydrology, on the origin and previous history of the samples or on the possibility and significance of recirculation.

(2) Accordingly, the composition of a given group of samples is regarded, in general, as a fairly good reflection of the composition of the adjacent geological formations and especially of the nature of local mineralization.

(3) Viewing believes that waters must be grouped according to the concentrations in them of all the major components. Furthermore, little importance is attached by him to the interpretation of the raw data *per se*. All data are expressed as ratios - the major components in the form of milliequivalent percentages and the trace element values as percentage fractions of total dissolved solids. Thus two waters differing only in Ca/Mg may fall into different groups, while two samples with very dissimilar TDS values may be placed in the same category. The casting of the samples into groups is done almost entirely on the basis of graphical methods of pattern analysis /155,285-94,320-1/ and practically no regard is paid to the geological setting of the sampling point. Examples of these patterns are reproduced in Figure D.

(4) Viewing divided the mine water samples into six groups. A concordance between his classification and that of the writer is given in Table D. The definitions of Viewing's groups are as follows /284/:

- I. "Water from country rocks - bicarbonate dominant, very low sulphate, Na + K, chloride".
- II. "Water from country rocks, modified in part, sulphates increased substantially but bicarbonate remains greater than sulphate. Na + K increases". According to Viewing, this modification is due to reaction of the waters from the country rocks with the orebody.
- III. "Mixed waters of the mine, sulphate exceeds bicarbonate and magnesium exceeds calcium".
- IV. "Mixed waters of the mine, sulphate exceeds bicarbonate but calcium exceeds magnesium".

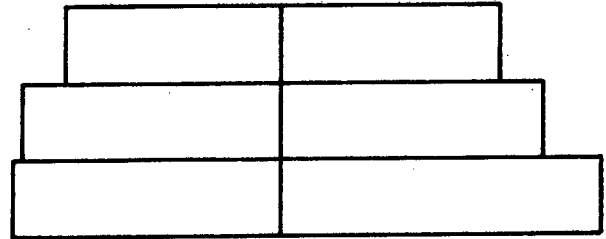
(Viewing did not give formal names to his last two groups. They are referred to here in terms of the symbols he used for them on his diagrams):

FIGURE D
 TWO EXAMPLES OF VIEWING'S PATTERNS
 fair drawn from his originals

SAMPLE NO. 138

	meq	%		meq	%
$\text{Na}^+ + \text{K}^+$	6,4	14,00	Cl^-	6,5	14,22
Ca^{++}	7,7	15,95	HCO_3^-	4,8	17,06
Mg^{++}	7,8	17,06	$\text{SO}_4^{=}$	9,5	20,78
TOTAL	47,01		TOTAL	52,06	(99,07)

TYPE III



SAMPLE NO. 132

	meq	%		meq	%
$\text{Na}^+ + \text{K}^+$	6,9	15,33	Cl^-	6,3	14,00
Ca^{++}	8,1	18,00	HCO_3^-	6,1	13,55
Mg^{++}	7,1	15,77	$\text{SO}_4^{=}$	10,5	23,33
TOTAL	49,10		TOTAL	50,88	(99,98)

TYPE "BLACK DOT R"

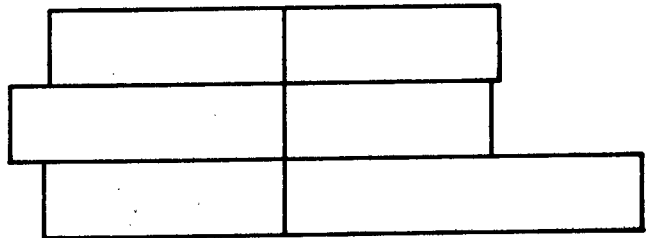


TABLE D

A COMPARISON BETWEEN VIEWING'S CLASSIFICATION OF THE TSUMEB MINE WATER SAMPLES
AND THE CLASSIFICATION ADOPTED IN CHAPTER FOUR OF THIS THESIS

Viewing	Sample	Chapter 4	Remarks
I.	162	IB	All fairly dilute waters found at shallow to very deep levels
	139	IIA	
	152	IIF	
	149	IIE	
	153	IIE	
II.	156	IIC	Viewing's group II is roughly equivalent to (IIC + IID)
	131	IIC	
	133	IIC	
	134	IIC	
	135	IIC	
	164	IIB	
	136	IIC	
	150	IIC	
	151	IID	
	144	IID	
147	IIA		
III.	160	IA	Mixed group
	145	IIA	
	140	IIA	
	138	IIB	
	165	IIC	
IV.	143	IA	Viewing's group IV corresponds well with a subset of IIB
	146	IIB	
	141	IIB	
	142	IIB	
	157	IIB	
	159	IIC	
Black dot	155	IA	Viewing's group "Black dot" corresponds with another subset of IIB
	166	IIB	
	132	IIB	
	158	IIB	
Black dot R	163	IA	Includes half of the IA samples
	161	IA	
	137	IIB	
	154	IA	
	148	IIB	

Group *Black Dot R*: "Mine waters, Ca greater than Mg and sulphate exceeds bicarbonate as does chloride in samples"

Group *Black Dot*: "Water from old stopes and mine workings, sulphate exceeds bicarbonate which is at a minimum. Mg greater than Ca".

(5) The classification of mine waters according to the abovementioned scheme is the basis for the recognition of anomalous ("mineralised") samples, irrespective of the trace element content. For example, Type I is regarded as "unmineralised", while Types III and IV are thought to be of great importance in terms of exploration *anywhere* in the Tsumeb-Grootfontein district. Noting that these two groups correspond very well with the waters that the writer regards as most altered by recirculation, the extent of the difference between the two interpretations becomes apparent.

(6) Viewing did not formally record his evaluation of the trace element data and other measurements such as pH and temperature. An examination of his diagrams suggests that he regarded the following as significant in hydrogeochemical exploration at Tsumeb: pH, $\text{SO}_4^{=}$, Cd, Zn, Hg, Se, Cl^- , Mn & Te.

APPENDIX E

An introductory description of the Tsumeb orebody and mine workings

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B. Lithology	E 2
C. Mineralogy and grade of the ore	E 3
D. Mining methods, history and present activities	E 7
E. Hydrological and hydrogeochemical data	E 8

APPENDIX E

An introductory description of the Tsumeb orebody and mine workings

This sketch of the mine is intended only to provide a backdrop to the hydrogeochemical orientation. Readers requiring additional information about the orebody are referred to publications /67,233,1169-70/ and /1172/. Many of the features discussed in this appendix are illustrated in Figures 1 and 2 and Maps 2 and 3, all of which are in Volume II.

(A) STRUCTURE AND SITUATION

The Tsumeb orebody is a vertical, pipelike structure /52,67,207,233/ that can be visualized as a distorted, elongated cylinder. The outline of the body is in detail quite irregular and the area of cross-section through the cylinder varies appreciably as the body pinches and swells along its length, which is at least 1700m. Most plan sections through the body approximate to an ellipse, with the east-west axis up to twice as long as the north-south axis, which is usually between 20m and 100m in length. Between 8 and 19 levels, however, the ratio of the short to the long axis becomes so large that the pipe is often more tabular than elliptical in shape.

The pipe is situated on the northern flank of an open syncline in the Tsumeb Stage of the Otavi Series (Section I of text). The original surface expression of the pipe, which was removed by open-casting, was about 250m stratigraphically below the base of the Mulden quartzite. It is not known how much of the original pipe was removed by erosion before the present land surface was established.

Figure 1 shows some of the detailed divisions of the Tsumeb Stage, which has eight zones. The pipe initially follows the southward dipping dolomites near the contact between zones 7 and 6, to a point about 650m below surface. Here it turns downwards and becomes a nearly vertical structure transgressive to the stratigraphy. At about 1200m below surface (35-36 levels) the pipe bends back briefly to follow the dip again, but almost immediately turns downwards once more to become perpendicular to the bedding. It continues in this manner as far as the structure has been proved (1975) by deep drilling, which has reached to 1700m below surface.

Throughout its length the pipe is quite sharply divided from and does not much disturb the surrounding country rock. Cylindrical fractures are commonly observed around the pipe, especially below 20 level. An important

structural feature of the host rocks is a major bedding plane fracture in Zone 6, which is called the North Break Zone. The Break descends from the surface and can be traced through and around the orebody. The dolomite along the Break is altered by brecciation, calcitization and manganese mineralization. The kink in the pipe structure at 35-36 levels is associated with a major bedding shear.

(B) LITHOLOGY

Figure 1 is a geological long-section through the Tsumeb metal deposit and it gives a good general picture of the major lithological units that occur in and around the pipe. (Important information about the construction of this long-section is given in Appendix C). The diagram depicts a simplified lithological classification, which combines certain distinctive varieties of carbonate rocks occurring within the core of the structure. The principle rock types within the pipe are massive ore, pseudo-aplite, graphitized dolomite, calcitized dolomite, silicified dolomite, massive calcite and dolomitic breccias. The interpretation of the origin and nature of the components of the pipe is controversial. Three important examples follow:

- (1) Pseudo-aplite has the composition of an arkose and exhibits other sedimentary features but is frequently intrusive. Opposing schools interpret it as either (a) an igneous intrusive (an unfashionable view at this time) (b) a diapirically mobilized sediment from within the dolomitic succession (c) a tectonically mobilized body of arkosic sand introduced into the pipe from the surface via very ancient karstic fissures.
- (2) Geologists who have worked in the mine differ about the extent to which one can correlate the altered dolomites of the pipe with the unaltered, adjacent country rock dolomites outside the pipe. In some cases there is evidence that they are indeed the same rock but, generally speaking, the relationship between the two classes of dolomites has not yet been established.
- (3) The breccias are accorded great significance by geologists interested in the genesis of the Tsumeb orebody, which is commonly regarded as a Breccia Pipe. Where typically developed, the breccia consists of elongated, angular fragments of dolomite, chert, altered dolomite and pseudo-aplite in a matrix of altered dolomite, pseudo-aplite and massive ore. The fragments are generally about 30 cm in diameter but can exceed two metres. The borders of the breccia bodies may be sharp or transitional. It has been variously suggested that these bodies are the result of (a) shock associated with igneous intrusion (b) collapse brecciation due to solution (c) low temperature tectonic shattering.

The various rock types of the pipe form elongated, irregular and usually vertically-orientated bodies that interlock in a complex of pinch and swell patterns. (Although the present tense is used for convenience, the description given here is of the pipe as it was originally. Much of its contents has already been excavated). These bodies are not randomly distributed throughout the pipe. The massive ore, for example, tends to form a cylindrical panoply around the periphery of the pipe structure. Massive ore and graphitized dolomite become rarer below 33 level and are absent towards the lowest levels, where silicified dolomite is more commonly seen. The main occurrences of brecciation in the pipe are confined principally between 24 and 39 levels, although other occurrences are known, for instance above 6 level. Pseudo-aplite is common in the upper part of the pipe, is rarer between 35 and 41 levels, and then reappears strongly at 44 level. Calcitized dolomite is much more abundant above 35 level than below it and the massive calcite body is practically confined between 32 and 36 levels.

Small kersantite dykes, which are very probably of Karoo age, cut through the pipe at 2 level and between 16 and 19 levels.

(C) MINERALOGY AND GRADE OF THE ORE

The patterns of distribution of minerals, grade, tonnage and minor components of the ore are quite complex, but some generalizations can safely be made. Data may be lacking for the deepest levels, which have not yet been intensively studied.

(i) *Distribution of oxide and sulphide zones*

Oxide minerals are very common down to about 300m below surface, although sulphides are not absent here. A sulphide-rich zone exists between 300-800m but below this, starting roughly from the intersection of the pipe and the North Break Zone, is another major oxide zone /1173/. The proportion of oxide minerals appears to be decreasing again towards the lowest levels. This unusual state of affairs has given rise to two theories. The classical view /67/ is that the ore was originally largely sulphidic and that alteration has occurred as a result of the circulation of oxidizing vadose water. These oxygen-rich fluids not only affected the ore near the surface but also gained access to deeper parts of the deposit via the North Break Zone. It seems certain that this mechanism has operated at least on the ore near to the present land surface, because supergene enrichment has taken place there. A more recent view /233/ is that much of the oxidic ore may have been deposited *per se* by late-stage, oxidic, hydrothermal

fluids.

(ii) *Grades and tonnages*

Data for grades and tonnages are given in Table E1. Between the surface and 30 level the ore is consistently rich, averaging better than 15% metals over most sections. The tonnage of ore is fairly regularly distributed along the pipe over this distance. Both the grade and the tonnage deteriorate markedly between 31 and 41 levels and there appears to be very little ore between 41 and 44 levels. Drilling suggests that the situation improves lower down. Something like $3, n \times 10^7$ tonnes of ore may eventually be removed from the Tsumeb deposit; something like two thirds has already been won.

In addition to the massive ore, almost any of the rocks of the pipe and even the adjacent country rocks may be mineralized /52,67,236/ to a greater or lesser degree. This mineralization consists of disseminated stringers and blebs and is sometimes of mineable grade. The massive calcite body is an exception, for it contains nothing more than sub-grade galena mineralization. Throughout the orebody the elements lead, copper and zinc preponderate. The approximate average concentrations in the ore are Pb 15%, Cu 6% and Zn 7% but the abundances and relative proportions of the metals vary considerably from place to place.

(iii) *General mineralogy of the ore*

Although the distributions of the ore minerals have been logged and many samples of ore have been analyzed, the vast mass of raw data has not been summarized in a form that would be of use to the geochemical prospector.

The massive ore contains from 30 to 60% metals. The principal minerals are galena (PbS), sphalerite (ZnS) and tennantite ($\text{Cu}_3\text{AsS}_3, 25^{\pm}\text{Zn}$), with subordinate chalcocite (Cu_2S), and bornite (Cu_5FeS_4). Pyrite is a common accessory mineral. Disseminated ore in pseudo-aplite commonly consists of bornite, chalcocite, digenite (Cu_9S_5) and galena. Disseminated ore minerals in dolomite are usually tennantite, galena, renierite ($(\text{Cu}_3\text{Ge,Fe})\text{S}_4$) and germanite ($\text{Cu}_3(\text{Ge,Fe,V})\text{S}_4$).

Whatever the dominant minerals happen to be in any particular region, the mineralogy of the ore is always complex. Dozens of other ore minerals may occur in accessory amounts and essentially monomineralic accumulations are unknown. Gangue minerals are predominantly dolomite, calcite and quartz, with accessories such as kaolinite, zeolites and, in the pseudo-aplite, feldspar.

Galena occurs throughout the mine. Sphalerite (a variety containing

TABLE E1

DISTRIBUTION OF Cu, Pb, Zn, Cd, Ag AND Ge IN THE TSUMEB MINE

Level	Cu%	Pb%	Zn%	Cd%	gram/tonne Ag
12	6,86	13,22	12,82	0,53	70,4
13	5,34	14,05	15,07	0,46	67,1
14	6,41	14,48	8,15	0,21	84,0
15	5,21	15,10	7,48	0,11	47,8
16	3,48	14,96	7,76	0,22	70,2
17	4,05	16,86	8,37	0,18	39,8
18	4,69	17,20	7,98	0,23	77,1
19	4,96	11,63	6,22	0,25	92,5
20	6,69	17,28	8,12	0,17	92,0
24	2,75	15,06	6,25	-	-
26	2,4	14,2	4,5	-	-
28	5,9	16,4	3,7	-	-
30	9,6	11,4	3,2	-	-
32	5,4	7,8	1,9	-	-
34	3,4	8,7	2,1	-	-
35	3,9	6,0	1,7	-	-
36	2,2	7,4	1,0	-	-
37	3,4	5,2	1,2	-	-
38	4,3	5,2	2,0	-	-
39	4,9	6,7	2,3	-	-
40	4,6	2,9	1,5	-	-
41	2,3	0,9	0,7	-	-

Data for germanium: Above 20 level : 0,17%
 21-27 levels : 0,13%
 28-30 levels : 0,11%

Values given are average grades for the whole level or, in the case of Ge, a group of levels.

Values for Cu, Pb, Zn, Cd and Ag between 12 and 20 levels calculated to a 5% cut-off grade. All other values calculated to a cut-off of 3,5% total metals.

about 2% cadmium and little iron) is also ubiquitous. The sphalerite:galena ratio is about 2:3 v/v. Tennantite is widely distributed and is certainly the principal copper mineral below 33 level. Chalcocite occurs on most levels, increasing in abundance from surface to 16 level, decreasing to 24 level and then increasing again to 30 level. Bornite is scarcer than chalcocite and is found especially in the upper levels. An exceptional concentration of both bornite and chalcocite occurs in the vicinity of the North Break between 29 and 30 levels. Germanite and renierite occur irregularly. A large mass of germanite was found above 6 level and good concentrations of germanium also occur at about 30 level.

As a result of oxidic alteration, an amazing variety of secondary minerals occurs in the mine, especially in the upper levels. Here the common minerals are chalcocite, carbonates of copper, lead and zinc, lead sulphate, copper-lead arsenates and vanadates. Examples are malachite ($\text{Cu}_2(\text{OH})_2(\text{CO}_3)$), azurite ($\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$), cerusite (PbCO_3) and descloizite ($\text{Pb}(\text{Zn,Cu})(\text{VO}_4)(\text{OH})$). As expected, the effects of leaching and supergene enrichment are seen in the upper levels. For example copper and lead are highly concentrated between surface and 6 level, while zinc is depleted. Nevertheless some sulphides such as galena and sphalerite have survived here in small amounts.

(iv) Distribution of elements within the Tsumeb pipe

Some of the features of the distributions of certain metals can be deduced from the foregoing discussion of the mineralogy of the orebody.

There is no simple, systematic, vertical or horizontal zoning of metals within the pipe. Copper, lead and zinc are common everywhere, except for minor pockets in which one or the other is relatively scarce. It is doubtful that these fluctuations have any significance from the point of view of hydrogeochemistry. There is little additional information concerning the distributions of most of the minor components of the ore (Cd, Ag, Ge, As and V). Germanium is the exception; the distribution of this element in the mine was studied by Frondel and Ito (1957 /1174/), who found that it occurred almost everywhere - mainly in solid solution in primary minerals such as tennantite, but also in a variety of secondary, oxidized compounds such as bayldonite and mimetite. Silver, arsenic and perhaps vanadium are also likely to be widespread, because they occur both in discrete minerals or by substitution in the more common species. Cadmium is found in sphalerite, which is ubiquitous. It is therefore probably safe to say that there is no massive concentration or depletion of any of these five minor elements at any particular level in the mine.

Virtually nothing is known of the distribution and occurrence of the uncommon and trace elements such as Ni, Cr, Te, Se, Li, Rb and Sr. The only exception known to the writer is the observation that mercury mineralization is confined to the North Break region of the pipe.

(D) MINING METHODS, HISTORY AND PRESENT ACTIVITIES

The aim of this subsection is to give the reader some idea of how long and to what extent various parts of the mine have been subjected to influences that might be of consequence in a hydrogeochemical study of minewaters, e.g., dewatering, breakage of rock, influx of air and cementation.

Except for some early open casting, classic cut and fill methods have always been used to remove ore in the Tsumeb mine; i.e., the cavities resulting from the removal of the ore are systematically filled up again with waste. A level is developed by driving an elliptical haulage around the outside of the pipe (Map 3 and Fig. 2). Secant cross-cuts (x-cuts) are driven across the pipe between the north and south haulages. The ore is accessed laterally from the x-cuts. Stopes are typically about 16 x 50 m in plan, are elongated north-south and are separated from one another by walls ("pillars") about 10m thick. The stopes are excavated upwards into vertical chambers and at the same time the floor is filled. The process stops when the base of the stope on the level above is approached. When two adjacent stopes on the same level are exhausted the pillar between them is removed by the same cut and fill method. A little ore is always left behind.

The principal fill materials used nowadays are waste rock from the drives and "red fill", which is a slurry of clayey soil and cement that is piped down from the surface. Various amounts of timber and steel are buried with the fill. However, the oldest stopes between surface and 6 level were filled with "waste" that is now regarded as good ore (1,5% Cu, 3,9% Pb, 0,7% Zn, plus some As and Ag). This material is still there and consists of a loose and usually coarse mixture of fragments of rock, copper-lead arsenates, vanadates, malachite, azurite, cerusite and small amounts of galena and sphalerite. In addition there is, between surface and 7 level, a substantial tonnage of unmined ore (2,6% Cu, 1,1% Pb, 0,8% Zn), which in the early days was regarded as being sub-grade.

Mining began around the turn of the century. The mine had reached 6 level by 1914 and this level was still being worked in 1921-2. Levels 13 to 16 were being mined in 1927-8. By 1938 twenty level had been opened. By 1947 the levels above number 12 were exhausted, the ore between 12 and 16 levels was reduced by half and active stoping was under way between 16 and 20 levels. In 1951 production started on 24 level and in 1957 on 30 level.

The ore on levels 30 to 34 was outlined around 1966 and development of the Seven Shaft levels (36 to 45) began around 1970.

Today the orebody is practically exhausted above 26 level. All the stopes are filled and there is little human activity here. The development of haulages etc. has been completed as far down as 35 level and stoping is presently in progress between 26 and 33 levels; most of the people in the mine are on these eight levels. Below 35 level the pipe is almost intact and the ore is practically pristine, except for a network of diamond drill holes. There is partial development outside the pipe on 36, 37, 38 and 44 levels but on all other levels below number 38 there is practically nothing other than drives between Seven shaft and Six shaft. The deepest development in 1975 was at 46½ level, some 1590 m below De Wet Shaft Bank.

The mine is generally wet and warm and under these conditions it can be very difficult to operate instruments such as pH meters. Steel, comminuted ore and other sources of trace metal contamination occur everywhere. Movement between levels is very difficult because the shafts are extremely busy and it is not practical or safe to climb the shaft manways with samples and sampling equipment.

(E) HYDROLOGICAL AND HYDROGEOCHEMICAL DATA

The few data that were available before this thesis study consisted mainly of measurements of water flow and hydrostatic pressure and some chemical analyses. Originally the water table in the area stood very near the surface and from the earliest times the control of water in the mine was a serious problem. The water table is much lower now, as a result of pumping, but the control of water is still a critical prerequisite to any new development. A system of preventative cementation has been used for many years. Holes are drilled ahead of any developing face or shaft in order to test the pressure of the water and to force in a cement mixture to seal any aquiferous fissures. A truly fantastic mass of cement has been used for this purpose over the years. For example, in a backup program of cementation in April and May 1953, which provided additional dewatering cover for the De Wet Shaft area between 22 and 33 levels, at least 26 200 pockets of cement were injected into the dolomite around the shaft. Cementation has of course been most intense in the lower levels, especially below 26 level, where hydrostatic pressures are greatest. In many areas the rock near the pipe, shafts and drives can be regarded, lightheartedly, as a dolomitic breccia with a cement matrix. The presence of this network of cement in the vicinity of potential sampling points has two important consequences:

(1) One must exercise caution in attempting to draw conclusions about the

natural hydrological regime from observed movements of groundwaters. After all, the *raison d'être* of cementation is to block the flow of water. Some deep boreholes flow rather slowly, yet develop great hydrostatic heads when sealed off. One must conclude that many freely flowing sources are not in equilibrium with the real pressure in adjacent groundwaters because of the friction caused by constricted paths of flow.

(2) It is possible that this mass of cement has had an influence on the chemical composition of certain groundwaters.

In 1973 the mine was being dewatered at the rate of 19 megalitres per day. This represented the average inflow from seepage and all mining operations including filling. This continuous pumping has produced a cone of dewatering at the mine, the apex of which was in the vicinity of 23 level in 1973. The cone is undoubtedly steep, but little can be said about its shape, except that it is irregular. Disequibrated, perched water tables are probably common in the levels above the main mass of groundwater, which probably does not have a well-defined water table surface. Certain zones, such as the North Break, are recognized as particularly good aquifers but sporadic inflows of water occur on many levels, particularly on the northern (up-dip) side of the pipe. Measured water pressures tend to increase with depth, but not regularly. Table E2 shows the figures for yield and pressure at control boreholes in the mine, as *reported* in February, March and April 1975. The writer has examined all similar records for the period 1960 to 1975, and local rainfall data, but found it impossible to draw any useful conclusions about the rates or timing of recharge. There is some slight indication that the deeper boreholes feel the effect of recharge some months after the rainy season, but one has to be very careful about attributing reported changes in yield and pressure to recharge when one has no knowledge of other factors that may be involved.

The highest pressures recorded in the mine, in the vicinity of 44 level, are around 134 atmospheres, which is equal to a hydrostatic head reaching to within a few levels of the surface. Since the apex of the cone of dewatering is at 23 level, this leaves little doubt about the importance at deeper levels of obliquely transferred hydrostatic pressure operating down dip. Thus it is probable that the water pressures in some strata may be more a function of stratigraphically channeled head than a function of the vertical distance to the water table directly above. The questions of yield and pressure become even more complex on the southern side of the orebody, where the inflow of water is less commonly observed and the relatively impervious pipe is interposed between the sampling point and the updip strata.

What is certain is that the mine workings are a region of relatively

TABLE E2

PRESSURES AND YIELDS REPORTED FOR UNDERGROUND BOREHOLES IN FEB. TO APRIL 1975

Hole		Yield in litres/sec			Pressure in KPa		
		Feb.	Mar.	Apr.	Feb.	Mar.	Apr.
2187P	26	4,3	4,3	4,3	2620	2620	2620
2555	26	34,0	40,8	40,8	2620	2620	2620
2559	27	8,2	8,2	-	2965	2965	-
2077	28	0,9	0,9	0,9	-	-	-
2821	30	19,0	25,5	25,5	5517	5517	5517
2855	30	51,0	51,0	51,0	5517	5517	5517
2864	30	40,8	40,8	40,8	5517	5517	5517
2915	30	40,8	40,8	40,8	5517	5517	5517
2908	30	40,8	40,8	40,8	5517	5517	5517

low pressure and that groundwater will tend to flow into it wherever it can do so. Water within the workings will generally have very little opportunity to flow back into the country rock against the hydrostatic head of the groundwater. It is possible that some water in the workings above 23 level may be able to move back into the country rock via dry fractures or other channels and then re-enter the mine a few levels further down.

Most of the water that enters the mine gravitates to sumps and is pumped to the surface. Some of it is treated and used in the water supply of the town. Some is used for mixing the red fill slurry and is returned to the mine in this manner. A large volume of raw mine water is used in milling operations and ends up in the slimes dams (Fig. 1 and Map 2). Waste water from the town is directed to the sewage works and irrigation scheme, about a kilometre west of the slimes dams.

To what degree water pumped from the mine sumps and discarded on the surface recirculates back into the mine workings by penetrating through the dolomites, is discussed in Appendix H. There is little doubt that some bodies of mine water contain a significant proportion of recycled water. This is important, because recycling tends to build up the concentration of ions such as sulphate, chloride and sodium and may affect the abundances of some minor components in the waters associated with the ore.

The few chemical analyses of mine waters that are regularly performed are for the purpose of examining the quality of the water entering the treatment plant and, occasionally, of testing the potability of the sources of drinking water underground. These data are summarized in a general way in Chapter 2. The composition of the mine waters is broadly similar to that of the regional groundwater; i.e., almost neutral in pH, with a moderate concentration of dissolved solids, and having as dominant components the ions calcium, magnesium, sodium, bicarbonate, sulphate and chloride. The raw mine water differs from the local groundwater principally in that it has relatively high concentrations of sulphate and chloride, a trace of cyanide (from the mill via the fill) and significant amounts of metals such as lead and copper, which are predominantly in suspensions rather than in solution.

APPENDIX F

Principles governing and experiments related to the choice of analyte elements and other parameters for observation and determination in hydrogeochemical orientation studies in the Otavi Mountainland

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A. Theoretical considerations	F1
B. Experimental studies	F1
C. Conclusion	F4

APPENDIX F

Principles governing and experiments related to the choice of analyte elements and other parameters for observation and determination in hydrogeochemical orientation studies in the Otavi Mountainland

(A) THEORETICAL CONSIDERATIONS

The need for basic observations such as temperature, pH, rate of flow in the case of mine waters, geological setting etc. is self-evident.

The selection of analytes and methods was governed by two factors:

(i) The samples were aqueous, dilute and of simple matrix. The majority of determinations was likely to be at concentrations of only a few micrograms per litre.

(ii) It was desirable to work with methods and equipment already available in the laboratories at Tsumeb Corporation Limited (TCL) or at the University of Cape Town (UCT).

This meant the use of routine wet chemical methods for most of the major components, atomic absorption spectrophotometry (AAS) for most of the trace elements, and x-ray fluorescence spectrometry (XRFS) and optical spectrography in certain special instances.

Due consideration was given to the possible role in hydrogeochemical exploration of each of the elements of the Periodic Table. (The Period Table appears in several forms and the one adopted in this thesis is depicted on the inside of the front cover of the volume containing the main text).

It was decided that

(i) Most of the elements of the Periodic Table are unsuitable for theoretical or practical reasons and were eliminated according to the logic of Table F.

(ii) The abovementioned analytical methods would be used to determine the remaining elements and any other species, such as ions that might conceivably be of some use in hydrogeochemical exploration. This included most of the better-known trace elements and all of the commonly occurring natural aqueous ionic species with the exception of nitrate, nitrite, borate and cyanide; these ions are known to have very low background concentrations in Tsumeb mine water /52/ and have no expected significance for prospecting purposes.

(B) EXPERIMENTAL STUDIES

These were of relevance mainly in the second part of the project, when waters from boreholes were collected and analyzed. As an additional

TABLE F
EXCLUSION OF SOME ELEMENTS OF THE PERIODIC TABLE AS PATHFINDERS IN WATERS OF
THE OTAVI MOUNTAINLAND

<i>Group</i>	<i>Elements excluded</i>	<i>Reasons</i>
IA	H	major component of water
	Fr	A
IIA	Be	B
	Ba	BaSO ₄ insoluble; A
	Ra	A
IIIB & IVB	All	A or B
VB	Nb and Ta	A or B
VIB	W	A or B
VIIB	Tc and Re	A
VIII	Ru, Os, Rh, Ir, Pd and Pt	A or B
IB & IIB	None	
IIIA	B and Ga	B
	In	A or B
IVA	Sn	A or B
	N	organic control over N makes its significance very doubtful
VIA	O	major component of water
	Po	A
VIIA	Br and I	C
	At	A
VIIIA	All	A or D
Lanthanides	All	A, B or C
Post uranic elements	All	A, B or D

Reasons:

- A. Natural concentration can be expected to be negligible.
- B. No hollow cathode lamp to hand. Expected concentration or significance does not justify the purchase of the lamp.
- C. Analysis not standard in the laboratories at TCL or UCT. Expected significance does not justify the development of the necessary techniques.
- D. Determination very difficult. Expected significance nil.

safeguard against the unlikely possibility that a potential hydrogeochemical pathfinder element had been overlooked, two tests were conducted in which optical spectrography /61/ was used to scan for any elements that were present, but had not been determined, in the water samples:

(1) In MIBK/APCD extraction the darkness of the extract is roughly proportional to the mass of extracted trace metals. The residues of about half a dozen of the darkest extracts obtained during solvent extraction of heavy metals (Appendix B4) from the borehole orientation samples were combined and arced. The only indication of any element other than those that had already been determined was a faint line at the gallium wavelength. It was likely that this was due to interference from iron. Gallium is in any case spectrally sensitive, rare and difficult to determine in microgram amounts and the matter was not pursued further.

(2) Not all elements are readily extracted into MIBK. As a further check on the completeness of coverage of the Periodic Table, two litres of water from a borehole near the Tsumeb mine (Vegetable Garden east-central, number 288; see Chapter 5) were acidified with Analytical Grade perchloric acid and evaporated to dryness, and the residue was mixed with sodium chloride and arced. The following elements were reported:

Confirmed: Mg, Ca, Na, K, Cu, Pb, Zn, Sr, Ag, B, Si

Doubtful : Ba, As

It is unlikely that small amounts (<50 µg/g) of the following elements would be detected in a scan of this type /208/: Ce, F, Gd, Hf, Hg, Ir, Nb, Os, P, Pt, Re, Sm, Ta, Te, Th and U. Of these, F, Hg, P and Te had already been determined in the orientation samples and the others are all rare and of little interest.

Additional investigation showed that the boron and silicon detected in the samples were very probably derived from the borosilicate glass in which the sample was evaporated. The As line was very faint and the identification very uncertain. Barium showed as only one weak line (4554,042 1000), which is unexpected for a cool, alkali-flooded arc. A portion of the evaporated residue was redissolved and analysed by AAS (Perkin Elmer 303 /281/) but barium could not be detected in this solution. Therefore, in order to obtain a detectable concentration of the metal, one litre of the original sample from borehole 288 was evaporated to 50 ml and analyzed by AAS along with a blank and standards. The original concentration of barium in the sample was found to be 0,07 mg/l and the detection limit of the method was 0,02 mg/l. It appeared that the element could not be detected without a six-fold or higher preconcentration. This represented a serious obstacle to any proposal to preconcentrate barium by evaporation because of problems caused by precipitation, matrix effects and non-atomic

absorption /28/.

Before consideration was given to the possibility of preconcentrating barium by ion exchange methods /28/, 18 of the orientation samples were selected for an additional study of the abundance of the metal. These samples included waters that were rich in sulphate, copper and zinc, as well as sulphate-poor, non-metalliferous waters from background situations. These were analyzed for barium by AAS, using a nitrous oxide/acetylene flame and a Cs-La dope /28/. The element could not be detected in any of the 18 samples. On the strength of the foregoing, and taking into account the fact that there is very little association of barium with local ores, it was decided that this element was of no significant interest as a hydrogeochemical pathfinder in the Tsumeb area.

(C) CONCLUSION

It was concluded that the coverage of the potentially useful elements of the Period Table was complete, and that the possibility of having missed a good pathfinder was remote.

APPENDIX G

Transportation, storage and utilization of samples

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APPENDIX G

Transportation, storage and utilization of samples

(A) UTILIZATION OF UNFROZEN SAMPLES FOR THE DETERMINATION OF MERCURY AND MAJOR COMPONENTS AND FOR OTHER WET CHEMICAL ANALYSES

The following were determined in the unfrozen samples: Mercury, phenolphthalein and methyl orange alkalinity, total and calcium hardnesses, total suspended solids (TSS), total dissolved solids (TDS), chloride, fluoride, manganese, chromium, phosphate and sulphate. (In the second phase of the project Mn and Cr were included with the heavy metals determined by AAS in frozen samples; see Appendix B). The more unstable components were determined first and the following order of procedure was adopted:

- (1) Determine mercury by AAS
- (2) Titration to determine P and M alkalinities
- (3) Titration to determine calcium and total hardnesses
- (4) Filtration to determine TSS. (The Millipore filter discs used were afterwards sealed in dustproof containers and kept for examination by XRFS).
- (5) Initial treatment of respective aliquots for the determination of manganese, chromium, phosphate, sulphate and TDS.
- (6) Titration to determine chloride
- (7) Completion of the analyses begun in (4) and (5) above.

The maximum time that elapsed between the collection of any mine water sample and initial treatment in the laboratory was eight hours. The data compiled in Appendix J show that it is most unlikely that serious deterioration of the samples would have occurred in such a short interval.

(B) STORAGE, TRANSPORTATION AND UTILIZATION OF FROZEN SAMPLES FOR THE DETERMINATION OF TRACE ELEMENTS

Deep-freezing is probably the surest method of preserving water samples for relatively long periods prior to trace element analysis /158-163,165-7,1147-8/. Orren /158/, Hendricks *et al.* /1146/ and others /1158-60,1162/ have recommended storage at either -10°C or -20°C . Borovitskii /1149/ stated that it was preferable, during groundwater hydrogeochemical prospecting for ores in Siberia, to do the field work in winter, when the samples froze spontaneously after collection.

This particular method of preservation is not generally used in exploration hydrogeochemistry because it is usually inconvenient to freeze large numbers of water samples rapidly. This was no problem at Tsumeb,

because the Municipality kindly allowed the writer to store his samples in the large deep-freeze chamber at the local abattoir. The temperature here is -20°C and samples placed along the walls were well iced within an hour. When frozen solid the plastic containers were stored in cardboard boxes. An air space was left in each bottle; none of them failed, and they could be reused repeatedly.

The first trace element determinations were made about two weeks after the last samples of mine water were collected. For these early colorimetric determinations one bottle of each sample was thawed by agitation and gentle warming in a water bath. Aliquots were drawn for the determination of arsenic and germanium, and initially for selenium and tellurium also. The remainder of the sample was immediately returned to the freezer and kept as a contingency reserve.

At this time (July 1973) TCL had not yet completed its new trace element laboratory and so arrangements were made to transport two litres of each frozen sample to the Department of Geochemistry at UCT, where a Varian Techtron AA6 had recently been installed. The samples were packed into boxes insulated with polyurethane sheeting and transported to Cape Town in 19 hours. The samples were still frozen solid upon arrival and were placed in a deep-freeze chest at -20°C .

Later the samples were thawed, shaken, split into several smaller aliquots in polyethylene containers and rapidly refrozen. One of these small containers was used for each group of trace element analyses described in Appendix B. The last analyses were completed within three months of collection of the samples.

At this juncture Tl, Mo, V, Sb and Bi had not yet been determined because hollow cathode lamps for these elements were not to hand in Cape Town. The lamps were available for the PE 303 instrument at TCL, but this does not have a carbon rod accessory. The best compromise appeared to be to use the 303 in conjunction with solvent extraction techniques to achieve the necessary sensitivity. These analyses were performed by the writer upon returning to Tsumeb. A sample container that had never been thawed was used for this purpose.

The metal content of the TSS residues was estimated by XRFS at UCT during 1973. The analyses were performed by the writer and were supervised by Dr. J. P. Willis.

APPENDIX H

The recycling of groundwater through the Tsuemb mine

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APPENDIX H

The recycling of groundwater through the Tsumeb mine

(A) INTRODUCTION

In attempting to understand the changes that occur in a groundwater that comes into close contact with a mineralized rock, it is important to know something about the previous hydrogeochemical history of that water. If the composition of the water is known before and after passing through the mineralized zone, then the net effects of the influence of the orebody are equal to the observed changes in chemistry.

It is especially important to monitor any changes in the composition of the groundwater that are due directly or indirectly to the influence of man, because industrial activity has the potential to alter the chemistry of natural waters to an extent unparalleled in either manner or degree in nature. If, in an orientation study, such unnatural effects pass unrecognized, then the chemical influence of the mineralized rock on the groundwater may be seriously misjudged and incorrect conclusions could be drawn about the usefulness of various hydrogeochemical pathfinders.

An important source of unnatural alteration of the geochemistry of groundwater is recirculation. Lane (1914 /1163/) recognized that the accumulation of sodium in mine waters could be due to recycling, which he termed "circulation". Handy *et al.* (1969 /1162/) described a more recent example of this phenomenon. The quality of groundwater in the Great Basin of Utah has deteriorated significantly as a result of "a high rate of pumping (and) a change in the chemical quality of the water that is recharging the aquifer". The content of dissolved solids and the concentrations of sodium and chloride, in particular, increased significantly during ten years of continuous pumping, usage on the surface and recharge through "infiltration of the excess water". They predicted that the quality "may deteriorate further because of local concentration (of salts) resulting from repeated reuse of groundwater".

It follows that hydrological factors must be stressed in any study of the hydrogeochemistry of mine waters that might have been recycled and reused. Whenever a mine is continuously dewatered there is always the possibility that some proportion of the water pumped to surface will penetrate back into the ground after being used or discarded, percolate back into the workings by various paths and be thereby recycled to some degree. This recirculation of groundwater is especially likely to occur in mines, such as the one at Tsumeb, where the bulk of the country rock is

dolomitic. The circulated water may not have the same composition as that of the local, pristine underground water and certain natural chemical equilibria existing between the rock and underground waters may, in consequence, be disturbed.

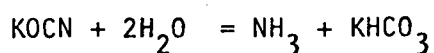
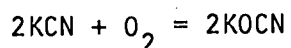
(B) CIRCUMSTANTIAL EVIDENCE OF RECYCLING: VARIATION OF THE QUALITY OF WATER WITH TIME

The possibility of recycling of groundwater used for a Municipal water supply has obvious socio-medical significance. Tsumeb Corporation is aware of the potential health hazard involved and constantly monitors the chemical and bacteriological quality of the water supply at all points from the underground sumps to domestic taps. The Corporation, sometimes in conjunction with the Department of Water Affairs and the Divisions of Health and Mining of the Administration /268/, has conducted studies of possible recycling into the mine of toxic, waterborne chemicals from the slimes dams (Map 2 and Fig. 1). The results have been uniformly negative; i.e.; no significant recycling of toxic species such as Cr(VI), As, Pb, Cd, Hg and cyanide can be discerned /52,268,271/. It does not follow that no circulation of *any species* is taking place. It remains possible that the water *does* recirculate and carries with it mobile ions such as sulphate and chloride, but that the less mobile components - including the toxic species- are effectively removed from solution by natural processes before the water re-enters the mine workings.

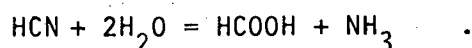
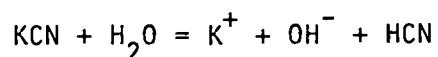
It is well known /49,51/ that the five elements listed above are no more than moderately mobile in solution even under favourable conditions. All except chromium are immobilized as carbonate. Chromium may be immobilized as the chloride, in ferric precipitates, on clays, and as several uncommon compounds such as lead chromate /41,61/; it is in general notoriously immobile. Cadmium is much less mobile than zinc under oxidizing conditions /802/ and is frequently left behind when zinc sulphide minerals are leached out of ores. Oxidizing conditions favour the precipitation of AsO_3^{3-} in the presence of iron. Mercury (I) chloride and sulphate are insoluble.

Korte *et al.* /1185/ showed experimentally that, relative to zinc, the elements Cr, As, Pb and Cd are all generally immobile in various types of soils. The data of Section III of this thesis provide additional evidence of the immobility of these elements in the waters of the dolomitic formations of the Otavi Mountainland.

Cyanides are intrinsically unstable under most natural conditions /274-5, 279-80/. They have some reducing properties and will be attacked by oxidizing agents such as free oxygen:



In addition, cyanides are saponified by atmospheric carbon dioxide /279/ and are readily hydrolyzed:



A number of other natural processes will destroy cyanides or convert them to ferricyanide, ferrocyanide and other complex forms /41,274-7, 280,1183/. Cyanides are also attacked by micro-organisms. *Actinomyces* will destroy more than 90% of cyanide present in concentrations from 25 to 100 mg/l /278/.

Alesii and Fuller /1183/ undertook an empirical study of the mobility of some forms of cyanide ions in various soils and claimed that cyanides are "very mobile in soils" /1184/. This claim is misleading. These authors saturated 10 cm columns of soils with up to 14 pore volumes of solutions containing 100 mg/l of cyanide. At the Tsumeb slimes dam the depth of soil and rock is three orders of magnitude greater, the volume ratio of cyanide solution to absorbant material is very much lower and the concentration of dissolved cyanide is twenty times less. Moreover, the abovementioned authors demonstrated that cyanide in real effluents is much less mobile than cyanide in solutions made up in distilled water. Their data in fact show that there is a severe initial retention of cyanide in most soils and that the ratio of cyanide input to cyanide transmission becomes significant only after two or three pore volumes of concentrated effluent have passed through the column of soil.

It follows that the absence of significant concentrations of cyanide or other toxic species in the waters of the mine sumps is no proof of the non-existence of recirculated mobile ions. It should, in theory at least, be possible to test this hypothesis by examining the records of chemical analyses of waters pumped from the mine over a period of several years. In practice this approach must be made with caution, because of the possibility of poorly-understood, extraneous influences that could be responsible for changes in composition that are not related to circulation. Examples are variations in rainfall over periods of several years, the dewatering of large, new sections of the mine and changes in the pattern of stoping with respect to the location of the sumps.

Table H1 summarizes analyses of Tsumeb bulk mine water between 1966 and 1975 /52/. Figure H1 shows the variations in the concentrations of sulphate and chloride in this water over the same period. The following is apparent from this data:

(a) There is no systematic increase in the concentrations of cyanide, lead, cadmium or arsenic. There are too few results for Cr(VI) from which to observe any trends and there are no data for mercury.

(b) The graph of $[SO_4^{=}]$ vs. time shows an irregular cycle. The sulphate content of the raw mine water was at an irregular maximum from 1966-68, then decreased to a minimum around 1970-71 and then began to increase once more. It seems that a systematic increase in the concentration of sulphate due to recycling, if it exists, is masked by other effects. The sulphate maximum of 1966-68 coincided with an intensive dewatering program that took place on 36 and 37 levels /52; Cilliers, pers. comm./ and it is possible that the two phenomena were connected in some way.

(c) The concentration of chloride shows a slow but definite and regular increase of about 100 mg/l/decade. It is clear that chloride and sulphate are not equally affected by the factors that control the concentrations of ions in the bulk water. This is emphasized by the cyclic variations shown by the sulphate/chloride ratio in Table H1. It is not unreasonable to ascribe the slow build-up of chloride ion to recirculation, because there is no evidence whatsoever of the existence of large, untapped, natural bodies of chloride-rich groundwater near the mine. If this interpretation is correct, then it follows that chloride is likely to be a better "natural hydrological tracer" than sulphate (cf. Chapter 4).

(C) CIRCUMSTANTIAL EVIDENCE OF RECYCLING: VARIATION OF THE QUALITY OF WATER IN SPACE

In October 1975 a comparison was made of the compositions of water samples collected from sources on the surface and underground. The samples were selected from bodies of surface waters that might be sources of recycled mine water and from underground boreholes that were likely to have relatively direct links with these surface waters (e.g., via the North Break Zone; Chapter 4 and Fig. 1). The data are compiled in Table H2 and are discussed below:

(1) Few of the high pressure boreholes listed here were included among the samples collected during the original orientation study of the mine waters. The reason for this is that the mine officials are very reluctant to allow the valves of these boreholes to be opened except in special cases, because of the danger of serious flooding should the valve become jammed in the open position.

TABLE H1

VARIATION IN THE COMPOSITION OF TSUMEB RAW MINE WATER WITH TIME (1966-75)

year	Cl ⁻	SO ₄ ⁼	KCN	Cd	As	Pb	SO ₄ ⁼ /Cl ⁻
1975	300	479	,003	,004	,06	,30	1,60
1974	266	428	,007	,015	,03	,20	1,61
1973	279	438	,005	,014	,02	,11	1,57
1972	280	411	,005	,007	,02	,20	1,47
1971	271	409	,002	,003	,01	,17	1,51
1970	244	407	,004	,007	,02	,09	1,67
1969	232	441	,009	,017	,04	,23	1,90
1968	218	464	,006	,003	,07	,46	2,13
1967	205	538	<,001	,015	,06	,54	2,62
1966		486			,06	,54	

All concentrations are in milligrams per litre.

Reported values are the means of all recorded analyses for the year. There are usually six determinations per annum.

TABLE H2. ANALYSES OF SELECTED SURFACE AND UNDERGROUND WATERS, OCTOBER 1975

Description of sample	borehole number	mine level	Na	Cl ⁻	Na/Cl	SO ₄ ⁼	CN ⁻	Cr(VI)	pH
High pressure borehole (North Break)	unknown	26	269	267	0,97	657	<,001	,004	7,5
High pressure borehole (North Break)	control 1	26	210	218	0.96	518	<,001	<,001	7,4
<i>Analytical control duplicate</i>			196	231	0,85	514	,001	,001	7,5
High pressure borehole (North Break)	control 3	26	136	146	0,93	335	<,001	<,001	7,9
High pressure borehole (North Break)	2209	26	240	231	1,04	594	<,001	,002	7,5
High pressure borehole (North Break)	unknown	30	214	243	0,88	503	<,001	<,001	7,6
High pressure borehole (North Break)	unknown	30	184	218	0,84	421	<,001	,002	7,5
High pressure borehole (North Break)	2822	28	200	231	0,87	575	<,001	<,001	7,6
High pressure borehole (North Break)	2988	27	270	255	1,06	701	,002	,002	7,5
High pressure borehole (North Break)	unknown	25	330	279	1,18	1104	,003	,002	7,5
Slimes dam, southern end	-	-	450	328	1,37	827	,350	1,08	8,5
Slimes dam, northern end	-	-	440	509	0,86	868	2,00	,540	9,0
Slimes dam, overflow vlei	-	-	570	534	1,07	1261	2,50	,450	9,0
Slimes dam, penstock overflow	-	-	406	425	0,96	829	3,85	2,430	9,0
Jordan river, dam	-	-	165	194	0,86	545	,002	,005	8,6
Jordan river, mine area	-	-	158	182	0,87	444	,002	,004	8,5
Leakage from fissure in roof	-	8	90	109	0,83	184	<,001	,017	7,6
Orebox	-	10	110	170	0,65	695	<,001	,005	8,3
Orebox	-	16	82	97	0,85	1047	,002	<,001	7,9
Manway	-	20	105	133	0,79	751	,001	,002	8,6

All results in mg/l. Analyses by TCL technicians using standard methods for the examination of effluents /10,17,52/. The Jordan river is a stream that runs westwards through the town of Tsumeb and then northwards past Reservoir hill to a dam (Map 2).

(2) Four of the boreholes listed in Table H2 were sampled during the original orientation work. Table H3 compares all the chemical data available for both samplings. The compositions of samples from sources in the upper levels of the mine changed little in the two year interval. The pH values are different, but this is probably because one set of values was measured *in situ* while the other was determined in the laboratory after a delay of a few days. The composition of the single sample from the North Break area has also remained quite constant, except for the sodium content, which appeared to rise significantly during the two year period. This apparent increase may have been caused by analytical error. On the other hand, it may be evidence of a slow migration of the boundaries that separate the different bodies of groundwater occurring near the pipe (Table 4.2 in Chapter 4 and Fig. 1f). It is possible that the uppermost portion of the body of type IIB water is being infiltrated by a sodium-rich water that may have some relationship to the nearby IIA waters, which are relatively enriched in this ion.

(3) Even if one disregards any deductions that might be made from the sodium data on the grounds that [Na] in certain bodies of TMW is changing with time (i.e., it may be impossible to differentiate between temporal and spatial controls on the concentration of sodium), one can accept with some confidence that the concentration of chloride is practically independent of time over periods of a few years and can therefore be used in making comparisons between bulk bodies of surface and underground waters. This is *not* a contradiction of point (c) in the foregoing subsection (B). Fig. H1 shows that the concentration of the chloride ion in the bulk mine water is increasing regularly, but *slowly*, so that nine years passed before the mean value had increased by 50%.

The chloride content of many TMW's, and especially the North Break waters that were labeled type IIB (Table 4.2), is remarkably high when compared to typical groundwaters anywhere in the Otavi dolomites in the districts of Tsumeb or Grootfontein. It seems very probable that recirculation within a hydrological system that is partially cut off from the regional groundwater system has contributed greatly to the high concentration of chloride. An estimate of the mass of chloride involved can be made as follows:

- (i) Assuming that the volume of dolomite occupied by the North Break waters is 1000 x 1000 x 500 metres and
- (ii) assuming that the mean porosity of this rock is 7% (subsection D, following), the mass of chloride-rich water may be set at 35×10^6 tonnes.
- (iii) Assuming that the mean concentration of chloride in these waters is equal to the mean value for all the North Break waters in Table H2 (232 mg/l), then it follows that the mass of dissolved chloride in this body of

TABLE H3

COMPARISONS OF THE COMPOSITIONS OF FOUR SOURCES OF TSUMEB MINE WATERS IN
1973 and 1975

	June 1973	Oct. 1975	Description
Na	161	240	Borehole. Sample number (1973) = 146. 26 Level, North Break Chloride water (Type IIB).
Cl ⁻	256	231	
Na/Cl ⁻	0,63	1,04	
sulphate	611	594	
pH	6,7	7,5	
Na	109	110	Ore box. Sample number (1973) = 154. 10 Level, Upper Level Stope water (Type IA).
Cl ⁻	130	170	
Na/Cl ⁻	0,84	0,65	
pH	7,2	8,3	
Na	94	82	Ore box. Sample number (1973) = 155. 16 Level, Upper Level Stope water (Type IA).
Cl ⁻	100	97	
Na/Cl ⁻	0,94	0,85	
pH	7,4	7,9	
Na	95	105	Manway. Sample number (1973) = 160 20 Level, Upper Level Stope water (Type IA)
Cl ⁻	103	133	
Na/Cl ⁻	0,92	0,79	
pH	8,2	8,6	

All concentrations are in milligrams per litre.

water is 8120 tonnes. This is not an excessive mass of chloride when one considers that (a) The chlorination of tapwater, without taking into account other sources of domestic and light industrial chloride, adds some 150 tonnes of the ion to the effluent circuit in a decade (Fig. H3) and has been doing so for about 40 years. (b) Ten million tonnes of typical Tsumeb ore contains 5 000 tonnes of chlorine (Table 4.6E). To date some 20-25 x 10⁶ tonnes of ore have been processed /52/ and much of the chlorine that was contained in it must have ended up in waste solution. (c) a large but uncertain mass of chlorine - probably of the order of $n \times 10^3$ tonnes - has been introduced over the years during cementation operations, mainly in the form of calcium chloride.

If this picture of slow, cumulative addition of chloride to what is practically a "closed circuit" groundwater recirculation system is correct, then one would expect to be able rationally to relate the chloride content of major underground aquifers to the chloride content of bulk water sources on the surface. For example, one could not hope to support the circulation hypothesis if the North Break waters had far more chloride than any surface water had.

An examination of Table H2 shows that the data do in fact fit the recirculation hypothesis. The slimes dam waters, suitably diluted, could easily be the source of all the sodium, chloride and sulphate in the North Break area. Similarly, the Jordan waters, with somewhat less dilution, can account for all the sodium and chloride (but not all the sulphate) in the waters of the Upper stopes (Type IA). The degree of dilution that is required in either case can be calculated from the means of the values for these three ions in the four principal types of water listed in Table H2 (i.e., Slimes dam-, Jordan-, North Break-, and Upper stope water). These data are compiled in Table H4. The results are entirely consistent with the hypothesis of recirculation and the provenance of certain bulk underground waters from specific sources of discarded waters on the surface. Sodium and chloride must each be diluted almost equally to produce North Break water from Slimes dam water, and *mutatis mutandis*, to produce Upper Stope water from Jordan river water. Note that the Upper Stope waters have more sulphate than can be supplied by the Jordan River. This is consistent with the hypothesis (Chapter 4) that there is a swift addition of sulphate to these descending waters from the broken and well-aerated ore in the upper levels. Note further that the sample from the fissure on 8 level (Table H2), which is thought by both the writer and the mine geologists to be a direct expression of some leakage on surface, is the only one of the samples of shallow water with less sulphate than the mean value for the Jordan river water.

TABLE H4

MEAN VALUES AND POSTULATED DILUTION RATIOS FOR SODIUM, CHLORIDE AND SULPHATE
IN FOUR PRINCIPAL TYPES OF SURFACE AND UNDERGROUND WATER

Mean values

	Na	Cl ⁻	SO ₄ ⁼
North Break Waters	224	232	594
Slimes dam waters	467	449	946
Jordan waters	162	188	495
Upper Stope waters	97	127	669

Dilution ratios

	Na/Na	Cl ⁻ /Cl ⁻	SO ₄ ⁼ /SO ₄ ⁼
(1) North Break/Slimes dam	0,48	0,52	0,63
(2) Upper Stope /Jordan	0,60	0,68	1,35

All concentrations in milligrams/litre

(4) The data of Table H2 show that the immobile species cyanide and Cr(VI), although present in significant amounts at the surface, are all but absent in the underground samples. This confirms the independent findings of TCL and Government Departments discussed on page H2.

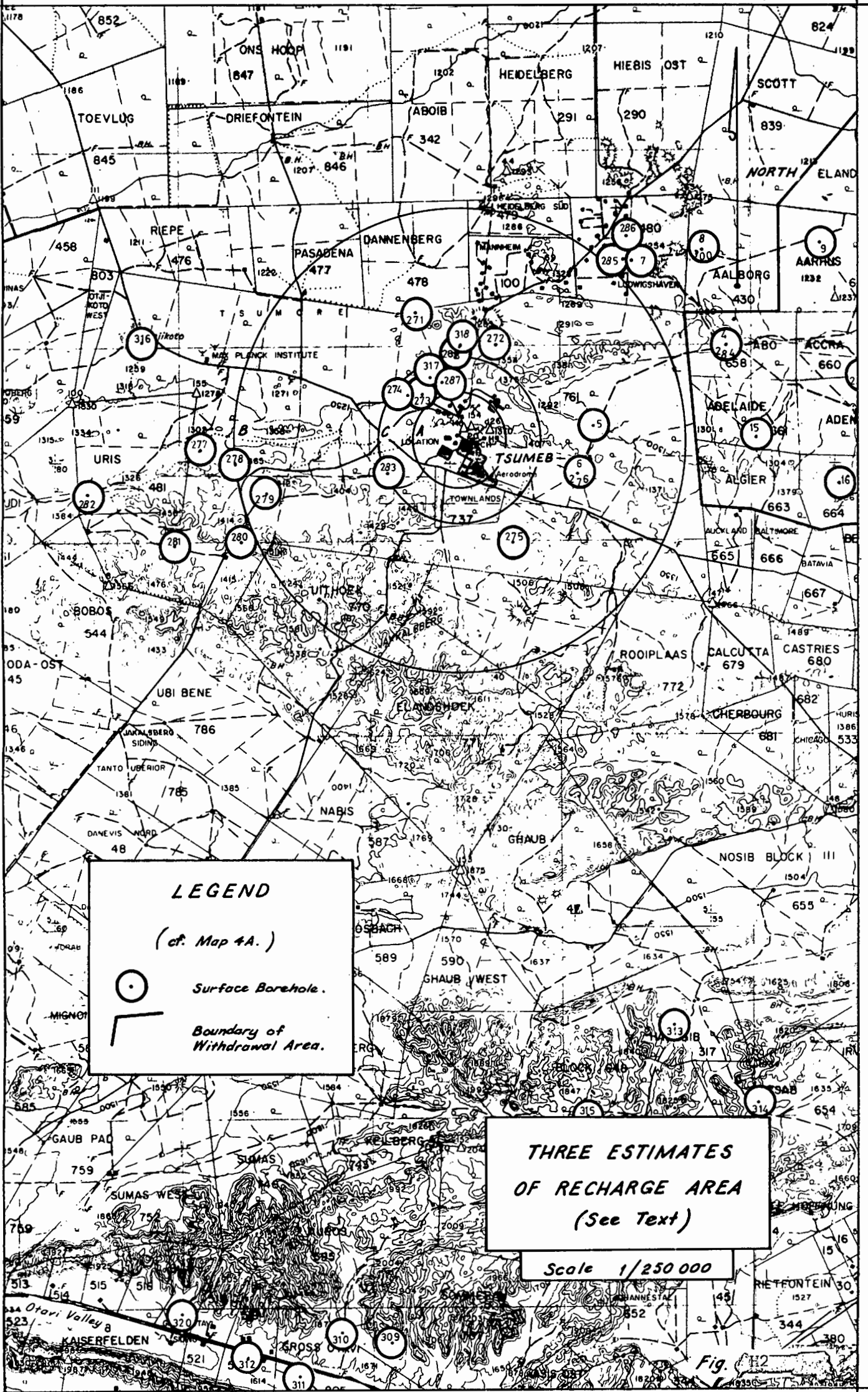
(D) CIRCUMSTANTIAL EVIDENCE OF RECYCLING: PUMPING - RAINFALL RECHARGE BALANCE

If the volume of water pumped out of the Tsumeb mine over several years greatly exceeds that which was replaced in that period by rainfall over a reasonable area around the mine, and no corresponding drop in the level of the local water table is noted, then some additional source of water supply is indicated. This may be recirculated water.


The calculation of a recharge balance for the Tsumeb mine is hindered by the fact that the available estimates of the recharge rate are in conflict with one another. Three estimates of this value are available and the calculations based on each of them are discussed, in turn, below:


(a) One opinion /272/ is that "very little (rain)water is lost as a result of surface evaporation and evapotranspiration" but no supporting data are given. Assuming that "very little" is 10%, then the following balance can be constructed: The average rainfall recorded in Tsumeb over 55 years is 530 mm/annum /268/. If only 10% of this is lost to evaporation then the recharge rate will be 477 litres per square metre per annum. The volume of water extracted from the mine is 8760 megalitres per annum. This volume of water could be replaced by recharge due to rainfall over an area of 18,36 km² in one year. A circular tract of this area has a radius of 2,42 km (Fig. H2, circle A). If the stated recharge rate is correct, then precipitation within a short distance of the mine is sufficient to account for all the water pumped during the year. This small circular area is practically co-extensive with the surface expression of the cone of dewatering of the mine. Since all boreholes within this area are dry, it is impossible to examine the effect of continuous pumping on the level of the water table within this area.

(b) Radioisotope experiments by the Department of Water Affairs have yielded a very different estimate of the rate of recharge. From limited carbon-14 dating of deep waters in the Tsumeb area a yearly increment of 30 cm is estimated /270/. The same source assumes that the porosity of the local rock is 3-10% and thereby estimates that 10-30mm of rain reaches the water table each year; i.e., 1,9% to 5,7% of the annual total of 530 mm as opposed to the 90% assumed in model (a) above. In order to repeat the calculations described in (a), it has been assumed that 20 mm (3,8% of the annual total) of the precipitation is added to the groundwater



LEGEND
(cf. Map 4A.)


Surface Borehole.


Boundary of Withdrawal Area.

**THREE ESTIMATES
OF RECHARGE AREA**
(See Text)

Scale 1/250 000

Fig. 12

reservoir. Under these circumstances the water pumped from the mine annually would be replaced by rainfall over an area of 438 km², or a circle of radius 11,8 km (Fig. H2, circle B).

This is a large circle, which encompasses several boreholes that are heavily pumped all year round without a systematic drop in the level of the water table being noticed. It is therefore unlikely that the mine is drawing groundwater away from an area as large as this. If the recharge estimates based on carbon-14 are correct, then considerable recirculation of water near the mine is indicated. It is of course possible that the recharge rate reduced from the radioisotope data has been biased by dry periods in the last few thousand years.

(c) The writer has attempted to derive an independent estimate of the recharge rate from a study of seasonal fluctuations of the water table recorded by the Department of Water Affairs in an (apparently) unpumped borehole at Otavi and in the Guinas and Otjikoto sinkhole lakes /270/ (Map 4). During the period October 1971 to June 1974 the maximum fluctuation in the Otavi borehole during any hydrological year (Nov.-Nov.) was 2,48 m. The derivation of a equivalent figure from either Guinas or Otjikoto is more complicated because both lakes are pumped for irrigation purposes. Nevertheless, these lakes are very well equilibrated with the regional groundwater table /273/ and a study of seasonal rather than short-term fluctuations will probably yield a reasonable estimate of the movement of the water table over the hydrological year. The writer's estimates, based on the raw data for the period May 1971 to March 1973, is 3m/annum for Otjikoto and 1,6m/annum at Guinas.

These three estimates of the seasonal fluctuation in the level of the water table are fairly similar considering the uncertainties involved. They are also in agreement with qualitative observations by the Department of Water Affairs of seasonal fluctuations of the water tables in 80 other boreholes in the Tsumeb karstic area /273/. For purposes of repeating calculations similar to those described in (a) and (b) above, the writer will assume that the observed fluctuations in the level of the water table are a direct function of the rate of recharge, and will assume further that the amount of recharge is the mean of the above three estimates of this variation; i.e., $(2,48 + 3 + 1,6)/3$ or 2,36 m/annum. It is also assumed that the mean porosity of the rocks is 6.5% (cf. (b) above). It follows that the amount of precipitation corresponding to the observed fluctuation (mean value) is $6,5 \times 2360/100 = 153$ mm or 28,9% of the annual total. The area over which the annual rainfall will replace the loss from the mine is then 57,1 km², or a circle of radius 4,26 km (Fig. H2, circle C).

This circle is much smaller than the circle produced by calculation

(b) but, unlike circle (a), it encompasses several heavily pumped boreholes. These, however, do not appear to be drying up as they might be expected to do if the recharge model (c) is correct and no recirculation of mine water occurs.

One must conclude that insufficient data are available to allow the construction of a highly reliable precipitation/recharge/extraction balance for the Tsumeb mine. Nevertheless, the balance of the evidence tends to support the hypothesis that a significant proportion of the mine water is being recycled locally.

(E) CIRCUMSTANTIAL EVIDENCE OF RECYCLING: PUMPING-DISPOSAL BALANCE

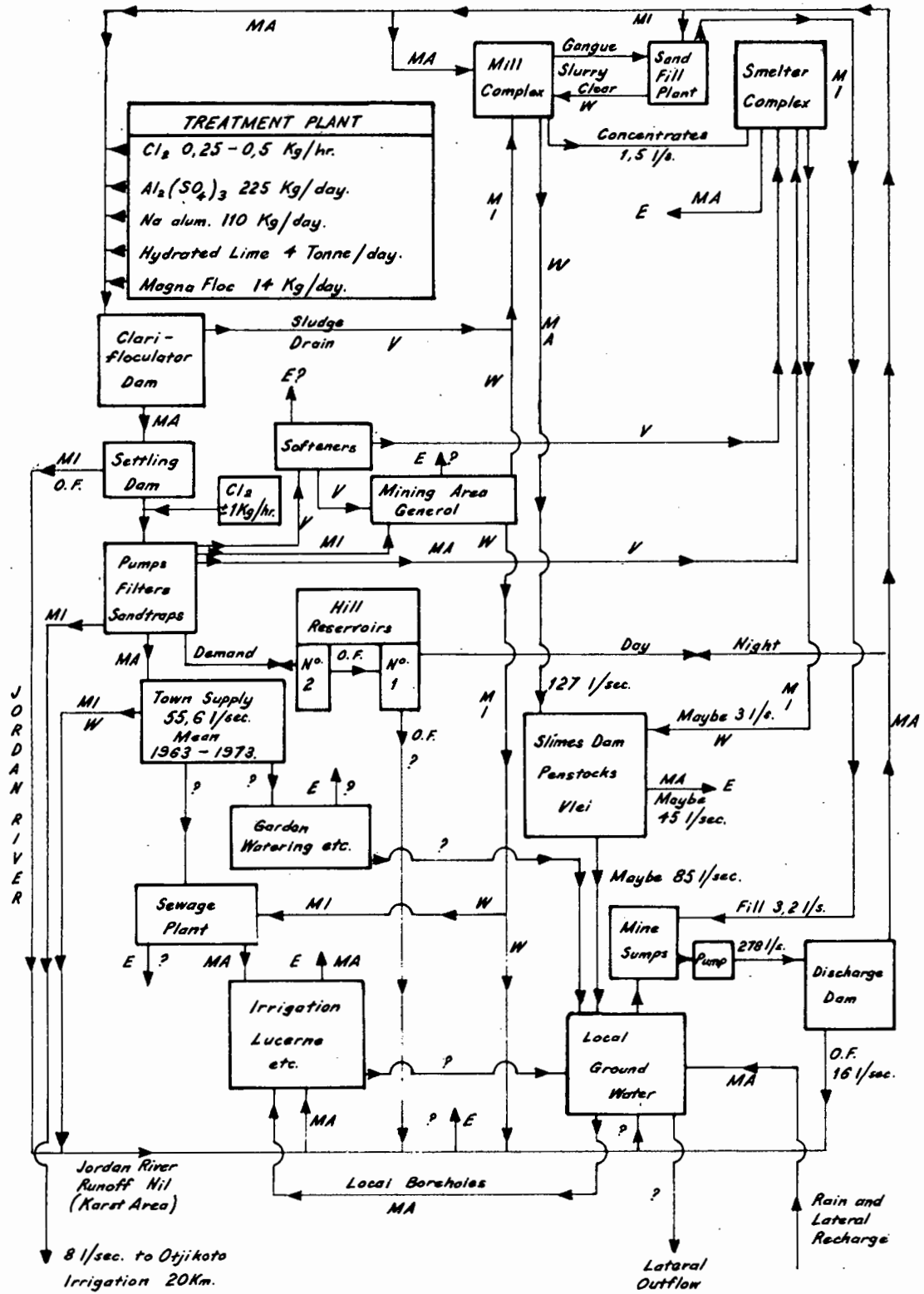
Another approach that may throw light on the question of recycling involves the construction of a pumping/usage/disposal balance for the water extracted from the mine. Some 24 million litres of water are pumped from the mine sumps each day. Can evaporation account for the disposal of all this water?

The Bulk Water Handling Scheme for the Tsumeb mine is summarized diagrammatically in Fig. H3 /52,268/. The locations of some of the features shown in Fig. H3 or mentioned in the text are indicated in Fig. 1 or Map 2. The Bulk Handling diagram shows the volumes of water delivered daily to various destinations or installations. Some of the values are very difficult to estimate and others are not well known, since there is a surplus of raw water and therefore little incentive to keep a detailed check on the volume delivered to every minor outlet.

Nevertheless the slimes dam complex is easily the most important depository for discarded water and eventually receives about half of the total volume of water extracted from the mine. An influx/evaporation balance for the slimes dam is calculated as follows:

The area of the slimes dams and associated penstocks etc is estimated to be $697\,792\text{ m}^2$ /52/. The mean annual evaporation figure for Tsumeb for the period 1959 to 1968 was $202,37\text{ cm}$ /269/. This was probably measured in a tank similar to the Symons evaporation tank, which is two feet deep /220/. Now the rate of evaporation over the open, shallow water layers of the dam will be somewhat higher than this. At most it will be doubled. But no more than half of the area of the dam is wet at any time, so for practical purposes these two factors can be assumed to negate each other. The mean volume of water evaporating from the dams each year is therefore estimated at $697\,792 \times 10000 \times 202,37 \times 10^{-3} = 1\,412\,121\,670$ litres per annum or $44,78$ litres per second.

The total influx of waste water into the dam (Fig. H3) is at least 130 l/sec . It seems that evaporation can account for only $34,5\%$ of this



LEGEND

MA Major Flow
 MI Minor Flow
 O.F. Over Flow
 W Waste Water
 ? Transfer Rate Unknown
 V Variable Transfer Rate
 E Evaporation and Evapotranspiration

N.B. All flow rates corrected for density.

TSUMEB BULK WATER FLOW CHART

volume and since there is no outflow from the dam, and the level is not rising, some 85 l/second must be soaking back into the ground. (This calculation ignores the effect of rainfall, which is equivalent to the addition of another 11,7 l/second to the area of the dam). Although the floor of the slimes dam is composed of very fine mud, it is apparently not impervious. There are obvious signs of the formation of vertical, subaqueous, erosional channels in the clay-rich sediments. Numerous sinkholes up to two metres across are visible in the floor of the vlei where the water is clearer. It is possible that large volumes of water could reach the bedrock via these channels, especially if they were coincident with solution cavities or fractures in the dolomite.

The calculated rate of recharge for the slimes dam area (85 l/sec.) is a minimum figure. To this must be added the unknown but probably relatively small contributions from the Jordan river, the sewage works, the irrigation scheme and domestic wastage. It does not follow that all of this water returns to the mine workings. However, it seems very probable that a significant fraction of the water does return to the mine via fractures, bedding planes and solution cavities in the dolomite. The North Break Zone, which is a very good aquifer, intersects the surface near the southern edge of the slimes dam and the prominent Huttenberg fault runs in a northerly direction under the dam. Both structural features may be implicated in the groundwater recycling circuit.

(F) CIRCUMSTANTIAL EVIDENCE OF RECYCLING: RADIOMETRIC DATING OF MINE WATER

It is very difficult to gain access to existing carbon-14 data for groundwaters in Namibia, but the seventeen analyses that were available to the author tended to confirm that the waters presently being pumped from the mines in the Otavi Mountainland are very young /1193/. The mean age of waters from the Kombat mine is only 18 years (range 0 to 70). The corresponding values for the Berg Aukas mine, near Grootfontein /189/, are 652 years and 0-1190 years. But the mean age of groundwaters that were collected from areas well away from any mine was 2220 years and the range was from 900 to more than 5000 years.

Unfortunately no data could be obtained for the Tsumeb mine. Nevertheless it is clear that the waters being pumped from the other two (similar) mines left the surface in the relatively recent past.

(G) DIRECT EVIDENCE OF RECYCLING

There is some direct evidence that fluids originating on the

surface are capable of seeping down and emerging on fairly deep mine levels.

(i) It was reported /TCL geologists, pers. comm./ that after diesel fuel leaked from storage tanks on the surface the oil worked its way through the dolomites and was observed to enter the developments, from fissures, on both 8 and 16 levels.

(ii) A TCL report /52/ states that "much more than 1 ppm" cyanide was detected in a borehole drilled from 20 level towards the north and which must have intersected the North Break, although the core furnished no unequivocal evidence of this. The location and orientation of this hole can be adjudged from Fig.1 and Map 2. It was drilled from near One shaft to a position roughly below the reservoirs on the hill above the town. The borehole was numbered 363 (diamond drill) and had a flat dip and an azimuth of 009° . It was drilled before 1950, and the co-ordinates of the collar were 1874E and 1999N in the Underground System. The purpose of the hole was to explore the North Break Zone at 20 level. The hole deflected upwards by 15 degrees and somewhat east and was therefore stopped at 332,2 metres, considerably short of the planned length of 550 metres. No mineralization was detected, but "red mud" issued from the hole around 330 m from the collar. A heavy flow of water was reported at 81,7 m.

The hole is now permanently sealed. The only feasible source for this cyanide is the slimes dam.

(H) CONCLUSIONS

The weight of circumstantial and direct evidence strongly suggests that large-scale recycling of groundwater is occurring via the North Break and the Upper levels of the Tsumeb mine. The influence of surface waters on the other water types found in the mine is less clear but there is a good possibility that they are also influenced by recirculation (Chapter 4). Recycling has caused an unnatural buildup of sodium, chloride and sulphate. It is very likely that this increased ionic concentration, together with accelerated rates of flow and ingress of oxygen, could have had important effects on the mobility and concentrations of less abundant species in the mine water. The implications of these possibilities are more fully discussed in Chapter 4.

APPENDIX I

*Experimental observation and calculation of the carbonic system parameters
in Tsumeb Mine Water*

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(C) LISTINGS OF COMPUTER PROGRAMS	123

APPENDIX I

*Experimental observation and calculation of the carbonic system parameters
in Tsumeb Mine Water*

(A) EXPERIMENTAL CONSIDERATIONS

The calculation of carbonic system variables will obviously inherit any uncertainties inherent in the experimental results used. Important aspects of the experimental methods used to estimate the primary carbonic parameters are summarized below.

(1) *Observed Alkalinity*

Observed Alkalinity is Total Alkalinity, the sum of the P and M alkalinities described in Appendix B3. It is defined as

$$A = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

The precision of the alkalinity titrations is generally better than 5%. The calculation of A from these figures is an approximation based on the assumption that the matrix of the sample is carbon dioxide-free distilled water, but is normally quite accurate. It is customary to express A in ppm calcium carbonate.

(2) *Observed concentration of calcium*

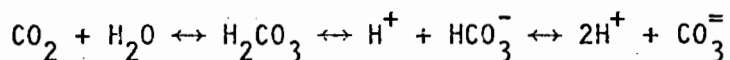
This value is calculated from the volume of EDTA titrated in the experimental method described in Appendix B3. Interferences in Tsumeb Mine water (TMW) are negligible and so the calcium data are generally of good quality. The calcium values are frequently expressed as ppm calcium carbonate.

(3) *Acidity, $p\text{CO}_2$ and the concentrations of carbonate, hydroxide and H_2CO_3*

The parameters acidity, $[\text{H}_2\text{CO}_3]$, $[\text{OH}^-]$ and $[\text{CO}_3^{2-}]$ all enter into the formulation of the carbonic equilibria. They are, however, difficult to obtain experimentally and are normally calculated from other experimental data by indirect methods. At the relatively low pH values found in TMW's the concentrations of hydroxide ion and carbonate ion are nearly zero.

The partial pressure of carbon dioxide is important in the carbonic

system because of the reaction



Nevertheless pCO_2 need not be measured experimentally because its influence is reflected in the values of pH and alkalinity. Many of the TMW samples collected from deep levels can be expected to be in equilibrium with concentrations of carbon dioxide well in excess of normal atmospheric pCO_2 , and will therefore have relatively low pH and high alkalinity values. Degassing from groundwaters entering the deeper workings probably contributes significantly to the high levels of carbon dioxide observed in the mine (Table 11)

(4) Observed pH

This measurement must necessarily be made *in situ*. At pH values around 6,5 to 7,2 (i.e., the range of values typical of TMW) the equilibrium state of the carbonic system is sensitive to small changes in pH (Fig. 11, in subsection (B) of this appendix). In order to predict the equilibrium parameters with high accuracy it is desirable to have pH data that are reliable to two decimal places. This was often impossible with the portable equipment that the writer was obliged to use.

Another experimental problem arose from the fact that it was not possible to measure pH directly at ambient pressure in deep boreholes. It follows that "observed pH" measured at low pressure at the sampling point may have differed from the pH of the parent groundwater reservoir. A drop in pressure affects pH in two ways:

(a) The apparent first and second thermodynamic dissociation constants for carbonic acid (K_1' and K_2') are pressure-dependent /334-5/. It is this phenomenon that is partly responsible, for example, for the accelerated dissolution of carbonate tests at depths below 3-5½ km in the ocean /47, 336-7/. Corrections for the effect of hydrostatic pressure will be discussed in subsection (B), following.

(b) The second effect of the release of pressure is indirect; the sample will tend to lose carbon dioxide and thereby change in pH. There appeared to be no way of making a quantitative estimate of how much carbon dioxide was lost while the sample travelled from the parent reservoir to the sampling point, and the writer has included errors from this source as part of the general uncertainty of pH determination. Fortunately the loss of carbon dioxide from solution is a slow process /23/.

The table of values of carbonic system parameters for TMW (Table 4.5 in the main part of the text) contains estimates of the probable error

TABLE 11

CONCENTRATIONS OF CARBON DIOXIDE IN AIR IN THE TSUMEB MINE

Level	Location	Range	Mean
34	Stopes	0,03-0,08	0,05
32	Development ends	0,05-0,15	0,08
30	"	0,05-0,09	0,07
35	"	0,05-0,15	0,08
37	"	-	0,10
44	"	0,03-0,08	0,05
36	"	-	0,05
12	Vent bypass	0,05-0,55	0,3
0-12	Various closed stopes		>0,5

All values are volume % carbon dioxide. The mean value for the atmosphere of the world is 0,03% /23/.

Data for the vent bypass recorded between Jan. 1971 to Dec. 1972. All other values recorded through 1973./52/.

due to uncertainty in the experimental value of pH. The error is given in terms of the corresponding uncertainty in the calculated value of the saturated concentration of calcium as ppm calcium carbonate.

(5) *Hydrostatic pressure*

Hydrostatic pressure must be known in order to correct the pH values of samples collected at great depths. The accurate measurement of pressure for each individual sample of TMW was impossible. Fortunately it was possible to obtain acceptable estimates of the pressures prevailing in various parts of the mine from records kept by the engineers at TCL /52/ (cf. discussion in Appendix E). The estimated pressures adopted for the orientation samples are compiled in Table 12.

(6) *Observed temperature*

It was unnecessary to allow for the small amount of cooling that may have taken place as the sample moved from the groundwater reservoir to the sampling point, because the carbonic equilibrium constants are but slightly sensitive to small changes in temperature. Measurements to the nearest half degree were quite adequate.

(7) *Ionic strength*

Ionic strength μ is defined /23/ as "an empirical measure of all ions in solution giving rise to deviation from ideal behaviour for chemical equilibria". The mechanism of this deviation can be visualized as a "shielding" of an ion from interaction with the bulk solution by a cloud of attracted ions of opposite charge. Ionic strength can be calculated accurately from the formula

$$\mu = \frac{1}{2} \sum C_n Z_n^2$$

where C_n is the molar concentration in the solution of the nth type of ion and Z_n is the ionic charge of that ion.

The values of μ for the TMW samples have been calculated using the values compiled in Chapter 3 for the concentrations of sodium, potassium, calcium, magnesium, sulphate, chloride and bicarbonate. The contribution of all other ions in these samples is negligible. Table 13 lists values of μ for the TMW samples and subsection (C) of this appendix contains the computer program that was used to calculate them.

TABLE 12

VALUES ADOPTED FOR HYDROSTATIC PRESSURE IN THE TSUMEB MINE WATER SAMPLES

Sample number	Atmospheres	Sample number	Atmospheres
1	100	19	134
2	100	20	114
3	100	21	124
4	104	22	138
5	104	23	134
6	111	24	1
7	76	25	1
8	80	26	94
9	86	27	90
10	80	28	90
11	76	29	94
12	86	30	2
13	58	31	1
14	127	32	42
15	5	33	5
16	73	34	104
17	66	35	97
18	73	36	97

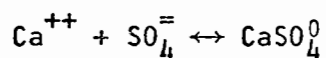
TABLE 13

Ionic strengths of samples of Tsumeb Mine Water

Sample	Ionic Strength
131	0,0320
132	0,0354
133	0,0245
134	0,0304
135	0,0286
136	0,0315
137	0,0455
138	0,0353
139	0,0199
140	0,0384
141	0,0341
142	0,0350
143	0,0372
144	0,0248
145	0,0287
146	0,0403
147	0,0266
148	0,0450
149	0,0161
150	0,0305
151	0,0253
152	0,0174
153	0,0156
154	0,0352
155	0,0526
156	0,0313
157	0,0427
158	0,0413
159	0,0356
160	0,0418
161	0,0357
162	0,0170
163	0,0263
164	0,0240
165	0,0357
166	0,0398

(8) *Effects of ion pairing*

In a consideration of the carbonic system in very dilute solutions the influence of reactions of the type



are of trivial importance /47/. As the concentration of the solution rises, however, an increasing proportion of each ionic species becomes dynamically bound in mutual ionpairs and these ions are removed from the population of reactive entities /338/. Loewenthal /23/ has shown that the effects of ion pairing in the carbonic system assume great importance only when the ionic strength exceeds 0,1 - a value well in excess of any observed in TMW. The influence of ion pairing has therefore been ignored in this study of the carbonic system in mine waters.

(9) *Transportation of samples*

Calcium and alkalinity were not determined at the sampling point but in a laboratory on the surface. These measurements are not affected by small changes in temperature that might occur during transportation from underground to a slightly cooler laboratory. The samples were also subjected to a small drop in barometric pressure (Table 14). This will have had no immediate effect on the samples and can be ignored, since all analytical work was completed within a few hours of collection. Note, however, that samples collected under these conditions cannot be stored for long periods prior to the determination of calcium and alkalinity; they will lose carbon dioxide slowly and will tend to precipitate calcium carbonate within about 48 hours of collection.

(B) CALCULATION OF THE CARBONIC SYSTEM EQUILIBRIUM PARAMETERS FOR TSUMEB MINE WATER SAMPLES

(1) *Introduction*

The object of these calculations, which will be described in detail in subsequent paragraphs, was to determine how close the observed state of a given sample was to the equilibrium or saturated state. The methods of calculation are based largely on the theoretical work of Loewenthal /23/, to whom the writer is greatly indebted for assistance and advice. The operations for the correction of fresh water carbonic parameters for

TABLE 14

ELEVATIONS ABOVE SEA LEVEL AND STANDARD BAROMETRIC PRESSURES IN THE TSUMEB
MINE

Level	Elevation	Pressure
Bank	1304	865
10	1027	894
20	728	927
30	343	971
38	33	1008

Elevations in metres above sea level. Pressures in millibars.

TABLE 15

RELATIONSHIP BETWEEN OBSERVED AND CALCULATED CARBONIC SYSTEM PARAMETERS IN THREE SITUATIONS: (1) OBSERVED VALUES AT LOW PRESSURE (2) "OBSERVED VALUES" AT HIGH PRESSURE (3) SATURATED VALUES AT HIGH PRESSURE

(1)		(2)		(3)
Low pressure observed parameter	Change from (1) to (2)	High pressure "observed" parameter	Change from (2) to (3)	High pressure saturated parameter
μ	none (note b)	μ	none (note c)	μ
T	assumed to be negligible	T	none	T
P	could be appreciable	P^1	none	P^1
pH	could be appreciable	pH^1	could be appreciable	pH^2
[Ca]	none	[Ca]	could be appreciable	[Ca] ¹
A	none	A	could be appreciable	A ¹
Acidity	none	Acidity	none	Acidity
K_1	could be appreciable	K_1^1	practically none	K_1^1
K_2	could be appreciable	K_2^1	practically none	K_2^1
K_w	could be appreciable	K_w^1	practically none	K_w^1
K_s	could be appreciable	K_s^1	practically none	K_s^1
fd	practically none	fd	practically none	fd
fm	practically none	fm	practically none	fm

NOTES:

(a) μ is ionic strength. T is temperature. P is hydrostatic pressure. Low pressure is taken as one atmosphere. The parameter Acidity, the four constants (K_x) and the divalent and monovalent activity coefficients fd and fm will be subsequently defined in the text. (b) $\mu = f(d\text{Volume}/dP)$ but is negligible below 1000 atmospheres. (c) The change in μ is negligible if the sample is not grossly disequibrated with respect to [Ca]. A change in [Ca] of 100 ppm CaCO_3 would change the operative value of μ by only 0,005 in a typical sample of mine water. An attempt to estimate $d\mu/d[\text{Ca}]$, where $[\text{Ca}] = f(\text{pH}, A)$, would result in an awkward differential equation.

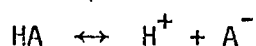
hydrostatic pressure were developed by Loewenthal and the writer and have not previously been published. The computer program for this task is reproduced in subsection (C) of this appendix. The input data are the known values for pH, A, calcium, temperature and hydrostatic pressure (Chapter 3 and Table 12) and previously calculated values for ionic strength (Table 13). The output is a comparative list of observed values and calculated, saturated (equilibrium) values for pH, A and calcium, for each sample, from which the degree of departure from theoretical equilibrium can be assessed (Table 4.5, Chapter 4). The various computations can be divided into two major operations:

- (A) Most experimental readings were made at a pressure of about one atmosphere, after the passage of the sample from the parent reservoir, which may have been at a much higher pressure. Some carbonic parameters will have been affected by this release of hydrostatic load. The first step was therefore to correct the pressure-dependent experimental data and dissociation constants for the change in pressure; i.e., to calculate what the "observed" parameters would have been had we been able to measure them directly within the parent groundwater reservoir. The computer program copes with this task in several steps: (i) Low pressure observed values of μ , T, A and pH are used to calculate low pressure dissociation constants for the carbonic equilibria and thus a value for low pressure acidity. (ii) Both alkalinity and acidity are independent of pressure /23/ and can therefore be transferred directly to the high pressure formulae as the "observed" values for these parameters. (iii) Using the observed values for P in the high pressure system, new values for the dissociation constants at high pressure are calculated. These new constants can be used to compute values for any other "observed" high pressure parameters.
- (B) The second step is to calculate what the theoretical concentrations of some carbonic species are within a given high pressure parent groundwater at equilibrium.

The saturated and "observed" high pressure data can then be compared. Table 15 is a summary of how the different carbonic parameters and constants may be affected by the operations described in A and B.

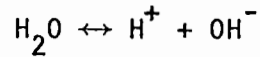
(2) *The calculation of dissociation constants and the effect on them of ionic strength and temperature*

The dissociation constant for any simple, ideal reaction of the type encountered in the aqueous carbonic system is defined, in the general case, by



$$[\text{H}^+][\text{A}^-]/[\text{HA}] = K_a^i \quad \text{.....(1)}$$

where HA is any weak acid and square brackets denote molar concentrations. The superscript i indicates that the constant applies to an ideal solution. The fundamental dissociation constants for the carbonic system are defined in this form in equations (2) to (5):

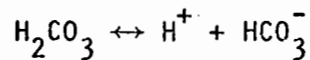


$$[\text{H}^+][\text{OH}^-]/[\text{H}_2\text{O}] = K_w^i \quad \text{.....(2)}$$

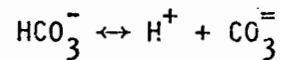
or

$$[\text{H}^+][\text{OH}^-] = K_w^i \quad \text{.....(3)}$$

since $[\text{H}_2\text{O}]$ remains, for all practical purposes, equal to unity.



$$[\text{H}^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3] = K_1^i \quad \text{.....(4)}$$



$$[\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-] = K_2^i \quad \text{.....(5)}$$

To apply the laws of mass action to non-ideal ionic equilibrium reactions, it is necessary to reduce the analytically determined molar concentrations of any reacting species by application of an activity coefficient. Active ionic concentrations are indicated by round rather than square brackets. In the general case

$$f_x[X] = (X) \quad \text{.....(6)}$$

where f_x is the activity coefficient of the xth type of ion. In non-ideal solution equation (1) therefore becomes

$$(\text{H}^+)(\text{A}^-)/(\text{HA}) = K_a \quad \text{.....(7)}$$

where K_a is the observed, non-ideal value for the dissociation constant for this reaction if active ionic concentrations are specified. Inserting the activity coefficients in the value of K_a and using molar concentrations, the general case becomes

$$f_{H^+} \cdot [H^+] f_{A^-} \cdot [A^-] / [HA] = K_a \quad \dots\dots (8)$$

HA is undissociated and its activity is unity. Upon rearranging,

$$[H^+][A^-] / [HA] = K_a / (f_{H^+} \cdot f_{A^-}) = K'_a \quad \dots\dots (9)$$

where the superscript ' indicates that K is the apparent constant for the reaction when deviations from ideal behaviour are considered and the ionic concentrations used are molar. Equation (3) may thus be rewritten

$$[H^+][OH^-] = K_w / (f_{H^+} \cdot f_{OH^-}) = K'_w \quad \dots\dots (10)$$

Many expressions have been proposed for the calculation of the activity coefficients. For reasonably dilute waters the most successful is the Davies equation, which yields values for f_x that depart from experimentally observed values by only 3-8% in solutions of ionic strengths 0,1-0,5 respectively:

$$\log f_i = -0,5 Z^2 \left(\frac{\mu^{1/2}}{1+\mu^{1/2}} \right) - 0,2\mu \quad \dots\dots (11)$$

and thus
$$f_i = 1/10^{\log f_i} \quad \dots\dots (12)$$

where f_i is the activity coefficient of a given type of ion i , Z is the ionic charge (valency) of that ion and μ is the ionic strength. This equation will be used to calculate monovalent ($f_i = f_m$ where $Z = 1$) and divalent ($f_i = f_d$ where $Z = 2$) activity coefficients for the samples of mine water.

The dissociation constants K_1 , K_2 and K_w are also dependent upon temperature and the functions defining these relationships are as follows: The Shadlovsky-MacInnes equation, for the range 0 to 38°C

$$pK_1 = (17052/T) + 215,21 \log_{10} T - 0,12675T \quad \dots\dots (13)$$

The Harned-Scholes equation, for the range 0 to 50°C

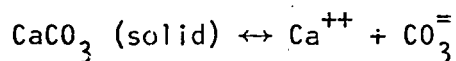
$$pK_2 = (2902,39/T) + 0,02379T - 6,498 \quad \dots\dots (14)$$

and the Harned-Hamer equation, for the range 0 to 60°C

$$pK_w = (4787,3/T) + 7,1321 \log_{10} T + 0,010365T - 22,801 \quad \dots\dots (15)$$

where T is in $^{\circ}\text{K}$ and $\text{p}K_1$, $\text{p}K_2$ and $\text{p}K_w$ are the respective negative logarithms (base ten) of K_1 , K_2 and K_w .

Also required for the calculation of the carbonic parameters at equilibrium is the temperature dependence of the active solubility product constant for calcite, $K_s(\text{CaCO}_3)$, usually abbreviated to K_s :



$$(\text{Ca}^{++}) (\text{CO}_3^{=}) / (\text{CaCO}_3) = K_s \quad \text{.....(16)}$$

and therefore

$$(\text{Ca}^{++}) (\text{CO}_3^{=}) = K_s \quad \text{.....(17)}$$

since the concentrations of the dissolved species at equilibrium are independent of the residual mass of solid calcium carbonate. The Frear-Johnston relationship can be expressed in the form

$$\text{p}K_s = 0,01183t + 8,03 \quad \text{.....(18)}$$

for the range 0 to 80°C , where t is in degrees Celcius.

With the foregoing equations one can calculate values for the various constants K'_x ; as in the following example, for K'_1 . Let the right hand side of equation (13) = R . Then

$$\text{p}K_1 = R$$

and

$$K_1 = 1/10^R \quad \text{.....(19)}$$

Equation (4) shows that the two ions involved are both monovalent and the other component is uncharged. Therefore, from equations (9) and (19)

$$K'_1 = K_1 / f_m^2 = (1/10^R) / f_m^2 \quad \text{.....(20)}$$

(3) Concepts and formulae pertinent to the calculation of low pressure acidity values

(a) Alkalinity (A) is defined as

$$A = 2[\text{CO}_3^{=}] + [\text{HCO}_3^{-}] + [\text{OH}^{-}] - [\text{H}^{+}] \quad \text{.....(21)}$$

In the alkalinity titration (Appendix B) this value is measured in terms of the concentration of strong acid (i.e. $[\text{H}^{+}]$) that is equivalent to the

masses of ions on the right hand side of the equation. A is normally expressed as ppm calcium carbonate, which means the concentration of CaCO_3 that is equivalent to the right hand terms. The alkalinity values for the mine waters (Chapter 3) must therefore be converted from ppm calcium carbonate to moles of H^+ before they can be used in the equilibrium expressions:

$$A \text{ as ppm CaCO}_3 = A/1000 \text{ g/l CaCO}_3 \quad \dots\dots(22)$$

$$= A/100000 \text{ moles/l CaCO}_3 \quad \dots\dots(23)$$

(the molecular wt. is 100)

$$= 2A/10^5 \text{ moles per litre H}^+ \quad \dots\dots(24)$$

since one mole of Ca^{++} is equivalent to two moles of H^+ .

(b) By similar reasoning

$$[\text{Ca}^{++}] \text{ in ppm CaCO}_3 = [\text{Ca}^{++}]/10^5 \text{ moles Ca}^{++}/\text{l} \quad \dots\dots(25)$$

(c) Experimentally determined pH is a measure of the *active* concentration of hydrogen ions in solution:

$$(\text{H}^+) = 1/10^{\text{pH}} \quad \dots\dots(26)$$

It follows from equation (6) that

$$[\text{H}^+] = (1/10^{\text{pH}})/f_m \quad \dots\dots(27)$$

(d) From equation (10)

$$[\text{OH}^-] = K'_w/[\text{H}^+] \quad \dots\dots(28)$$

(e) From equation (21)

$$[\text{HCO}_3^-] + 2[\text{CO}_3^{--}] = A - [\text{OH}^-] + [\text{H}^+] \quad \dots\dots(29)$$

and from equation (5)

$$[\text{CO}_3^{--}] = K'_2[\text{HCO}_3^-]/[\text{H}^+] \quad \dots\dots(30)$$

and therefore

$$[\text{HCO}_3^-] = (A - [\text{OH}^-] + [\text{H}^+]) / ((2K_2' / [\text{H}^+]) + 1) \quad \dots\dots(31)$$

(f) Acidity can now be calculated from the foregoing:

$$\text{Acidity} = 2[\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{H}^+] - [\text{OH}^-] \quad /23/ \quad \dots\dots(32)$$

from equation (4)

$$[\text{H}_2\text{CO}_3^*] = [\text{H}^+][\text{HCO}_3^-] / K_1' \quad \dots\dots(33)$$

and therefore

$$\text{Acidity} = (2[\text{H}^+][\text{HCO}_3^-] / K_1') + [\text{HCO}_3^-] + [\text{H}^+] - [\text{OH}^-] \quad \dots\dots(34)$$

With these equations it is possible to calculate any required low pressure carbonic parameter.

(4) *The calculation of the high pressure dissociation constants*

Relatively little has been written about the effect of pressure on the carbonic equilibria /43,339/. Most of the published material concerns seawater, since pressures above about 30 atmospheres are rarely encountered in studies of fresh water /43,339/. Apparently all recent work concerning high pressure aqueous carbonic systems has been for seawater models /340-3/; these results cannot be casually transferred to fresh water models /339/. Thus it appears that the standards work on the effect of high pressure in dilute aqueous carbonic systems is still that of Owen and Brinkley (1941 /334/). They showed that the pressure dependence of the equilibrium constants of ionic reactions is given quite accurately by

$$RT \ln(K^{(P)} / K) = (-\Delta\bar{V}^0)(P-1) + \frac{1}{2}\Delta\bar{K}^0 (P-1)^2 \quad \dots\dots(35)$$

for increments in pressure of the order of 100 bars, where R is the universal gas constant (0,08205 litre-atmosphere per degree /43/), T is absolute temperature, $K^{(P)}$ is the value of the equilibrium constant at the higher pressure, K is its value at one atmosphere, $\Delta\bar{V}^0$ is the volume change of the reaction under standard state conditions and $\Delta\bar{K}^0$ is the algebraic sum of the standard partial molar compressibilities of the products and reactants. Thus

$$K^{(P)} / K = e^{((- \Delta\bar{V}^0)(P-1) + \frac{1}{2}\Delta\bar{K}^0 (P-1)^2) / RT} \quad \dots\dots(36)$$

and

$$K^{(P)} = (K^{(P)} / K) (K) \quad \dots\dots(37)$$

Values for $\Delta\bar{V}^0$ and $\Delta\bar{K}^0$ are available from tables /334/ and those that are relevant to this appendix are reproduced in Table 16. It will be seen that some assumptions and approximations must be made in using this data but according to Loewenthal /339/ no serious errors are thereby introduced.

(5) *The calculation of "observed" high pressure pH values*

With the aid of the high pressure dissociation constants derived in paragraph (4) it is possible to compute the value of any "observed" high pressure parameter. A glance at Table 15 will show that the only important unknown in this category is pH; this value is obtained by taking the the observed (= "observed") values for Alkalinity and Acidity and solving for $[H^+]$. In general any of the low pressure equations detailed in the foregoing paragraphs (1) and (2) can be used in the high pressure model if the high pressure dissociation constants of the general form $K'_x(P)$ are substituted wherever the low pressure version K'_x previously occurred. Therefore, by substituting equations (28) and (5) into equation (21) and equations (4) and (28) into equation (32) we have

$$A = (2K'_2(P) \cdot [HCO_3^-]/[H^+]) + [HCO_3^-] + (K'_w(P)/[H^+]) - [H^+] \quad \dots (38)$$

$$\text{Acidity} = (2[H^+][HCO_3^-]/K'_1(P)) + [HCO_3^-] + [H^+] - (K'_w(P)/[H^+]) \quad \dots (39)$$

and

Rearranging equation (38) gives

$$[HCO_3^-] = (A - (K'_w(P)/[H^+]) + [H^+]) / ((2K'_2(P)/[H^+]) + 1) \quad \dots (40)$$

and substituting this into equation (39) yields

$$\text{Acidity} = \left(\frac{A - (K'_w(P)/[H^+]) + [H^+]}{(2K'_2(P)/[H^+]) + 1} \right) \cdot \left(\frac{2[H^+]}{K'_1(P)} + 1 + [H^+] - (K'_w(P)/[H^+]) \right) \dots (41)$$

This is a cubic equation but it can be simplified without significant error. At the pH values prevailing in Tsumeb mine waters $[OH^-]$ is negligible and terms representing the hydroxyl ion can be dropped. From equation (28) $[OH^-] = K'_w(P)/[H^+]$. Furthermore, $(A + [H^+])$ is very nearly equal to A alone. Thus we may write

$$\text{Acidity} = (A / ((2K'_2(P)/[H^+]) + 1)) \cdot ((2[H^+]/K'_1(P)) + 1 + [H^+]) \dots (42)$$

TABLE 16

SELECTED VALUES FOR $\Delta\bar{V}^0$ AND $\Delta\bar{K}^0$ FROM OWEN AND BRINKLEY /334/

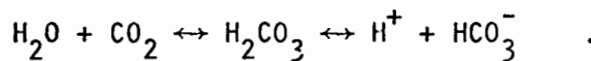
REACTION ^a	$\Delta\bar{V}^0$	$\Delta\bar{K}^0$ ^b
$\text{H}_2\text{CO}_3^* \leftrightarrow \text{H}^+ + \text{HCO}_3^-$ ^c	-29	<i>d</i>
$\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{=}$	-27,8	-87×10^{-4}
$\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-$	-21 ^e	-52×10^{-4}
$\text{CaCO}_3 \leftrightarrow \text{Ca}^{++} + \text{CO}_3^{=}$ ^f	-58,3	-157×10^{-4}

NOTES:

(a) The reactions are assumed to take place in pure water

(b) Values for $\Delta\bar{V}^0$ and $\Delta\bar{K}^0$ are at 1 bar and 25⁰ C unless otherwise stated. In most case data are not available at other temperatures. The unit of measurement of volume is cubic centimetres.

(c) The asterisk is the conventional method of indicating that what is actually meant by the above apparent reaction is in fact the total reaction



(d) Assumed to be negligible /334/.

(e) Extrapolated value for 40⁰ C. Variation between 25⁰ and 45⁰C about 12%.

(f) For calcite.

and

$$(\text{Acidity} \cdot (2K_2^{(P)} / [\text{H}^+])) + \text{Acidity} = (A \cdot 2[\text{H}^+] / K_1^{(P)}) + A + 2K_2^{(P)} + [\text{H}^+] \quad \dots (43)$$

and therefore

$$(2K_2^{(P)} \cdot \text{Acidity}) + (\text{Acidity} \cdot [\text{H}^+]) = \frac{2A \cdot [\text{H}^+]^2 + A \cdot [\text{H}^+] + 2K_2^{(P)} [\text{H}^+] + [\text{H}^+]^2}{K_1^{(P)}} \quad \dots (44)$$

and further

$$((2A/K_1^{(P)}) + 1) \cdot [\text{H}^+]^2 + (A + 2K_2^{(P)} - \text{Acidity}) \cdot [\text{H}^+] - 2K_2^{(P)} \cdot \text{Acidity} = 0 \quad \dots (45)$$

and therefore

$$[\text{H}^+] = \frac{(\text{Acidity} - 2K_2^{(P)} - A) \pm \sqrt{\{(A + 2K_2^{(P)} - \text{Acidity})^2 + 4((2A/K_1^{(P)}) + 1)(-2K_2^{(P)} \cdot \text{Acidity})\}}}{2((2A/K_1^{(P)}) + 1)} \quad \{\dots (46)\}$$

This equation, being of the general quadratic form

$$x = \frac{-b \pm \sqrt{b^2 + 4ac}}{2a}$$

has two roots. In Tsumeb mine water Acidity is larger than A (cf. equations (21) and (32) and the low values for $[\text{CO}_3^{=}]$ recorded in Chapter 3). Therefore $-b$ is positive and greater than 1 and so b^2 exceeds b . The term $4ac$ is negative and small because $K_2^{(P)}$ is small. The term $2a$ is positive. Therefore, in order to make $[\text{H}^+]$ positive, the plus option of the square root term must be adopted.

Finally, pH is obtained from the value of $[\text{H}^+]$ by rearranging equation (27).

(6) *The calculation of the high pressure saturated parameters pH, alkalinity and concentration of calcium ion*

(a) Introduction to the problem

Using the high pressure values for the dissociation constants and the high pressure "observed" value for pH it is possible to calculate the high pressure saturated values for pH, Alkalinity and $[\text{Ca}^{++}]$. This is not

a straightforward problem, however, and the difficulties involved are best illustrated by referring to Figure 11, which was provided by Loewenthal /23/. This figure is an example of a Modified Lawrence-Caldwell diagram (MLC diagram) which is produced by instructing the computer to draw the contents of a given "window" on the continuum of $(Alk - [Ca^{++}])$ vs. Acidity. The diagram has the following important features:

- (i) It is an *equilibrium* diagram and it applies only to a water of given ionic strength and temperature.
- (ii) The co-ordinates of the diagram are the values Acidity and $(A - [Ca^{++}])$; The expression Alk may be encountered instead of A as an abbreviation for Alkalinity. The concentrations on both axes are given in ppm $CaCO_3$.
- (iii) The axes enclose a field of lines of constant A, pH and $[Ca^{++}]$, which are the loci of selected solutions to the equilibrium equations for these three variable. Intermediate values can be obtained by interpolation.

The intersection of the appropriate A, pH and Ca lines uniquely defines the saturated state of any given water. For example, a water for which A is 200 and pH is 7,2 must have $[Ca^{++}] = 340$ ppm $CaCO_3$ at saturation. Let us assume that the water is in fact undersaturated and that the measured value for Ca is 290. It does *not* follow that equilibrium can be achieved by dissolving an additional 50 ppm $CaCO_3$; this is because the equilibrium state that is to be achieved is governed by three simultaneous equations, each of which must be satisfied at the new point of equilibrium. Any two or even all three variables may have to change before the new state of saturation is reached.

Obtaining a mathematical solution to the three simultaneous equations is complicated by the fact that at least one of them is cubic in most cases. The practical solution to the problem is to use an iterative method; this gives successive approximations of the values of pH, A and Ca that simultaneously satisfy the requirements of equilibrium and yet comply with the restraints imposed by the values for pressure-independent (conservative) parameters inherited from the low-pressure "model" for the particular sample under consideration.

The iterative procedure makes use of certain properties of the carbonic system that are implicit in the MLC diagram when certain physical conditions are met: *if* there exists a closed sample system, such as a mass of groundwater, *then* the only possible liquid-solid reaction that can occur during the transition from the disequilibrated to the saturated state is either the dissolution or precipitation of $CaCO_3$, *and then* the parameters $(A - [Ca^{++}])$ and Acidity are conservative because they are independent of ΔCa^{++} or ΔA . This conclusion may be understood by examining equations (17), (21) and (32); Acidity has no calcium or carbonate term and calcium and

IONIC STRENGTH= .0100 TEMPERATURE (DEGC)= 20.0
 APPROXIMATE TDS(PPM)= 400

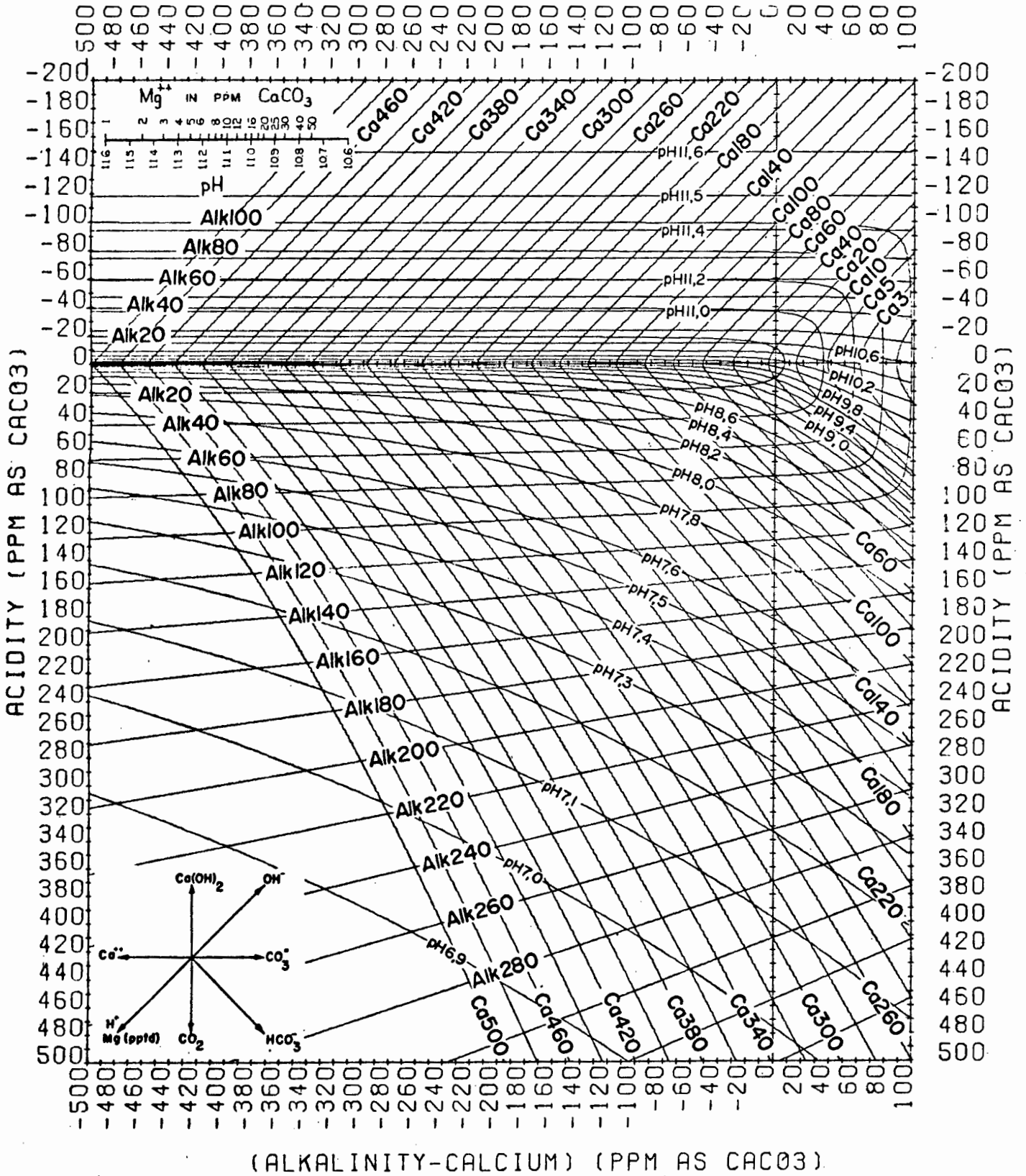


FIGURE 11. MODIFIED LAWRENCE-CALDWELL DIAGRAM

carbonate ions are removed from or added to the respective values A and $[Ca^{++}]$ in equal amounts.

Thus the goal of the iterative procedure is to find values for pH, A and Ca, computed with the high pressure dissociation constants $K'_X(P)$, that are mutually non-contradictory (i.e., that will plot as one point on the MLC diagram) and at the same time yield calculated values for Acidity and $(A - [Ca^{++}])$ that are equal to those already known to hold for the low pressure model. The iterative method will be discussed in paragraph (c), following. Before doing so, however, it is necessary to examine the derivation of some additional parameters required for the iterative procedure.

(b) Methods of solving for the high pressure values of $[OH^-]$, $[HCO_3^-]$, $[CO_3^{=}]$, $[Ca^{++}]$ and A

The procedures for solving for these five parameters are similar to those that were detailed in the foregoing subsections (2) and (3). The high pressure dissociation constants $K'_X(P)$ are substituted wherever the equivalent low pressure value K'_X previously occurred. For example, substitution in equation (28) of the high pressure value for $[H^+]$ (here designated $[H^+]^{(P)}$) and the dissociation constant $K'_W(P)$ gives

$$[OH^-]^{(P)} = K'_W(P) / [H^+]^{(P)} \quad \dots\dots(47)$$

The new value of $[OH^-]^{(P)}$ can then be used to compute $[HCO_3^-]^{(P)}$, and so on. The equations used (*mutatis mutandis*) are:

for $[H^+]^{(P)}$	number 27
$[HCO_3^-]^{(P)}$	31
$[CO_3^{=}]^{(P)}$	30
$[Ca^{++}]^{(P)}$	17
A ^(P)	21

(c) Detailed explanation of the iterative technique for calculating high pressure saturated values of A, pH and Ca

The simplest way of explaining the procedure is to work through the Fortran program reproduced in subsection (C) of this appendix.

(i) The following definitions are used: The high pressure saturated value for any parameter is indicated by a suffix-superscript (s); e.g., $pH^{(s)}$. Any approximation to this value that is generated by the computer during

the iteration is designated by a suffix-superscript (an); e.g., $\text{pH}^{(a)}$, $\text{pH}^{(a1)}$, $\text{pH}^{(a2)}$ etc. where the general case is indicated by (a) only and the first, second etc. approximations by (a1), (a2) etc. Any low pressure observed (\equiv high pressure "observed") values are designated by a suffix-superscript (L); e.g., $A^{(L)}$ and $[\text{Ca}^{++}]^{(L)}$.

(ii) $A^{(L)}$ and $[\text{Ca}^{++}]^{(L)}$ are known. $(A - [\text{Ca}^{++}])^{(L)}$ is calculated. (The expression used in the program is actually $A - 2[\text{Ca}^{++}]$, because the input data are in moles, whereas the MLC diagram used ppm CaCO_3).

(iii) A random number may be assumed for the first approximate high pressure saturated value of $\text{pH}^{(a)}$. In practice the first assumed value $\text{pH}^{(a1)}$ is set equal to $\text{pH}^{(L)}$, since this is likely to be a reasonably close approximation to $\text{pH}^{(s)}$ in many cases.

(iv) The first of three consecutive IF controlled loops is entered.

(v) Using $\text{pH}^{(a)}$, the high pressure dissociation constants, f_m and Acidity, the computer generates first approximate saturated values for the concentrations of H^+ , OH^- , HCO_3^- , $\text{CO}_3^{=}$, Ca^{++} and for A.

(vi) From this data the first value of $(A - [\text{Ca}^{++}])^{(a)}$ is calculated.

(vii) The value of $(A - [\text{Ca}^{++}])^{(a)} - (A - [\text{Ca}^{++}])^{(L)}$ is examined. *IF* the result is zero, control passes to the third loop. *IF* the result is positive, then $(A - [\text{Ca}^{++}])^{(a)}$ is too large. This can be remedied by decreasing $\text{pH}^{(a)}$ (cf. Fig. 11, noting the direction rose). The value of $\text{pH}^{(a1)}$ is therefore reduced by 0,1 to give $\text{pH}^{(a2)}$ and returned through the loop. The process is repeated until $(A - [\text{Ca}^{++}])^{(a)} - (A - [\text{Ca}^{++}])^{(L)}$ is either zero, whereupon control passes to the third loop, or negative, whereupon control passes to the second loop. *IF* the result is negative, control passes directly to the second loop

(viii) The second loop is always entered with a value of $\text{pH}^{(a)}$ such that $0,1 > (\text{pH}^{(s)} - \text{pH}^{(a)}) > 0$.

(ix) A variable called FRACT is defined to be 0,01 and $\text{pH}^{(a)}$ is now incremented by FRACT. The second loop repeats all the calculations that were executed in the first loop and generates another value for the

difference $(A - [\text{Ca}^{++}]^{(a)})$.

(x) The test $(A - [\text{Ca}^{++}]^{(a)}) - (A - [\text{Ca}^{++}]^{(L)})$ is repeated. *IF* the result is zero or positive, control passes to the third loop. *IF* the result is negative the value of $\text{pH}^{(a)}$ is incremented by FRACT and returned to the loop. The process is repeated until the result becomes non-negative, whereupon control passes to the third loop.

(xi) The third loop is always entered initially with a value of $\text{pH}^{(a)}$ such that $0,01 > (\text{pH}^{(a)} - \text{pH}^{(s)}) > 0$.

(xii) The last increment of FRACT is reversed so that $0,01 > (\text{pH}^{(s)} - \text{pH}^{(a)}) > 0$. FRACT is then set equal to FRACT/10 and control is transferred back to the start of the second loop. The value of $\text{pH}^{(a)}$ is now incremented in steps of 0,001 until $0,001 > (\text{pH}^{(a)} - \text{pH}^{(s)}) > 0$, whereupon control again passes to the third loop.

(xiii) The loop again divides FRACT by 10 and the second loop is again entered with $\text{pH}^{(a)}$ being incremented by 0,0001.

(xiv) This process continues until $|\text{pH}^{(a)} - \text{pH}^{(s)}| \approx 10^{-6}$, whereupon a counter at the end of the third loop breaks the cycle.

(xv) The final values residing under the variable names holding $A^{(af)}$, $[\text{Ca}^{++}]^{(af)}$, $\text{pH}^{(af)}$ etc. are such that the required simultaneous equations are satisfied and $(A - [\text{Ca}^{++}]^{(af)}) - (A - [\text{Ca}^{++}]^{(L)})$ is very nearly zero and $(A - [\text{Ca}^{++}]^{(af)})$ is very nearly equal to $(A - [\text{Ca}^{++}]^{(s)})$. The various final values $X^{(af)}$ are adopted as the values for $X^{(s)}$:

$$\text{pH}^{(af)} = \text{pH}^{(s)}$$

$$[\text{Ca}^{++}]^{(af)} = [\text{Ca}^{++}]^{(s)}$$

$$A^{(af)} = A^{(s)}$$

(xvi) The execution of the program is terminated after all cases (sets of sample data) have been processed.

(C) LISTINGS OF COMPUTER PROGRAMS

Listings of the two computer programs described in this appendix follow:

PROGRAM 1

THIS PROGRAM CALCULATES IONIC STRENGTH MU (U) OF WATERS,
FROM TOTAL MAJOR COMPONENT DATA, USING THE FORMULA:

$$U = 1/2 \text{ SUM } (C \text{ SUB } N) \text{ TIMES } ((Z \text{ SUB } N) \text{ SQUARED }) ,$$

WHERE (C SUB N) IS THE CONCENTRATION IN MOLES PER LITRE
AND (Z SUB N) THE IONIC CHARGE OF THE NTH IONIC SPECIES.

MARCHANT MAY 1976.

THIS PROGRAM HAS <61 LETTERS PER LINE SO AS TO FIT A4.

THIS PROGRAM IS WRITTEN FOR THE UNIVERSITY OF CAPETOWN
UNIVAC 1106.

DATA INP, IOP/8,5/

REAL MAJOR(14,1002)

THE ARRAY ' MAJOR ' WILL HOLD ALL DATA AND COMPUTED
RESULTS AND IS INITIALISED AS IN THE FOLLOWING EXAMPLE :

ARRAY MAJOR(I,J)

COL.	1	2	3	4	5	..N..	..I
	SMPL.NO.	SODIUM	CALCIUM	SULPHATE	CHLORIDE	ETC	ETC
ROW 1	XXXXX	XXX	XXX	XXX	XXX	XXX	XXX
2	YYYYY	YYY	YYY	YYY	YYY	YYY	YYY
3
ETC
.
J-2	ZZZZZ	ZZZ	ZZZ	ZZZ	ZZZ	ZZZ	ZZZ
J-1	BLANK	22.98	40.08	96.06	35.45	ETC	ETC
J	BLANK	1.	2.	2.	1.	ETC	ETC

NOTES:

- (1) ALL ANALYSES MUST BE IN MG/LITRE.
- (2) THERE ARE I VARIABLES INCLUDING SAMPLE NUMBER.
I MAY NOT EXCEED 14.
- (3) NO VARIABLE, INCLUDING SAMPLE NUMBER, MAY
EXCEED SIX CHARACTERS IN LENGTH.
- (4) THERE ARE (I-1) IONIC SPECIES.
- (5) THERE ARE (J-2) SAMPLES. J MAY NOT EXCEED 1002.
- (6) THE (J-1)TH ROW HOLDS MOLECULAR WEIGHTS FOR THE
RESPECTIVE IONIC SPECIES.
- (7) THE (J)TH ROW HOLDS THE IONIC CHARGE VALUE (Z)
FOR THE RESPECTIVE IONIC SPECIES. IGNORE SIGN
(POSITIVE OR NEGATIVE).
- (8) THE ANALYTICAL DATA IS NOT RECOVERABLE FROM THE
ARRAY. THE FINAL CALCULATED RESULT (U) IS
STORED IN THE SECOND COLUMN OF THE ARRAY.
- (9) THE FIRST DATA RECORD SUPPLIES VALUES FOR I AND

```

C          J, FORMAT 214 ( RIGHT JUSTIFIED ).
C      (10) THE SECOND DATA RECORD GIVES THE FORMAT IN WHICH
C          THE PRINCIPLE ANALYTICAL DATA ARE TO BE
C          PRESENTED. THERE MUST BE ONE SAMPLE PER RECORD,
C          GIVING SAMPLE NUMBER FIRST ( FORMAT A1 TO A6 )
C          AND FOLLOWED BY THE ORDERED ANALYTICAL DATA IN F
C          FORMAT.
C      (12) THE PRINCIPLE DATA PACK ( J-2 RECORDS, EACH OF 1
C          WORDS ) FOLLOWS.
C      (13) THE PENULTIMATE DATA RECORD GIVES (I-1) ORDERED
C          MOLECULAR WEIGHTS ( FORMAT (13F6.2) ).
C      (14) THE LAST DATA RECORD GIVES (I-1) ORDERED VALUES
C          OF Z ( FORMAT (13F6.2) ).
C
C          INTEGER A,B
C      A,B,L AND M ARE COUNTERS.
C          DIMENSION AFMT(16)
C      AFMT IS A DUMMY NAME FOR THE DATA FORMAT IN (10) ABOVE.
C          READ(INP,4)I,J
C           4 FORMAT(214)
C          READ(INP,10)AFMT
C           10 FORMAT(16A5)
C      THE FORMAT FOR READING IN THE PRINCIPLE DATA IS NOW
C      STORED UNDER THE NAME AFMT.
C      AN IMPLIED LOOP WILL NOW BE USED TO FILL (J-2) ROWS AND
C      (I) COLUMNS OF THE ARRAY ' MAJOR ' WITH SAMPLE DATA.
C          M=J-2
C          READ(INP,AFMT)((MAJOR(K,L),K=1,I),L=1,M)
C      SIMILARLY, THE REMAINING TWO ROWS OF THE ARRAY WILL BE
C      PARTIALLY FILLED WITH ( I ) MOLECULAR WEIGHT VALUES AND
C      ( I ) Z VALUES, RESPECTIVELY. THE REMAINING BLANK SPACES
C      IN THE MATRIX ARE IGNORED.
C          A=J-1
C          READ(INP,15)(MAJOR(K,A),K=2,I)
C           15 FORMAT(13F6.2)
C          READ(INP,16)(MAJOR(K,J),K=2,I)
C           16 FORMAT(13F6.2)
C      THE ARRAY IS NOW STOCKED.
C      IN A NESTED LOOP USING ONE ARITHMETIC EXPRESSION, THE
C      FOLLOWING WILL OCCUR TO EACH ANALYTICAL DATUM
C      ( MAJOR(X,Y) ) :
C      (1) THE VALUE IS DIVIDED BY 1000 TO CONVERT TO GRAMS
C          PER LITRE.
C      (2) THE RESULT IS DIVIDED BY MOLECULAR WEIGHT TO
C          CONVERT TO MOLES PER LITRE.
C      (3) THE RESULT IS MULTIPLIED BY Z SQUARED TO GIVE
C          (C SUB N) TIMES (( Z SUB N ) SQUARED ), WHICH
C          RESULT IS STORED BACK IN ( MAJOR(X,Y) ).
C          L=0
C          18 L=L+1
C             DO 20 K=2,I
C                MAJOR(K,L)=MAJOR(K,L)*10.0**-3.0*MAJOR(K,J)**2.0
C                */MAJOR(K,A)
C          20 CONTINUE
C             IF (M-L)22,22,18
C      USING A NESTED LOOP, THE (C SUB N)*((Z SUB N) SQUARED)
C      VALUES WILL BE SUMMED IN EACH ROW, FOR EACH SAMPLE AND
C      STORED IN THE SECOND COLUMN OF THE ARRAY.
C          22 L=0
C          25 L=L+1
C             DO 30 B=3,I

```

```
      MAJOR(2,L)=MAJOR(2,L)+MAJOR(8,L)
30  CONTINUE
    IF (M-L)32,32,25
C THE (C SUB N)*(Z SUB N) SQUARED) DATA WILL NOW BE HALVED
C TO GIVE MU (U).
    32 DO 40 L=1,M
      MAJOR(2,L)=MAJOR(2,L)/2.0
    40 CONTINUE
C THE CALCULATION IS COMPLETED. TITLES FOR THE OUTPUT WILL
C NOW BE WRITTEN.
    WRITE(10P,42)
C INSERT REQUIRED TABLE NO. IN THE FOLLOWING LINE
    42 FORMAT(1H1,28X,'TABLE ',///,18X,'IONIC STR'
      *,'NGTH OF TSUMEB MINE WATERS',///,23X,'SAMPLE NO. I'
      *,'ONIC STRENGTH')
C THE RESULTS WILL BE WRITTEN, WITH THE CORRESPONDING SAMPLE
C NUMBER.
    WRITE(10P,45)((MAJOR(I,L),I=1,2),L=1,M)
    45 FORMAT(1H ,29X,13,X,F6.4)
C THE FORTRAN PROGRAM IS COMPLETED AND WILL BE EXECUTED.
    STOP
    END
```

PROGRAM 2

C
 C
 C THIS PROGRAM CALCULATES IMPORTANT PARAMETERS PERTAINING TO
 C THE THEORETICAL EQUILIBRIUM (SATURATED) STATE OF THE
 C AQUEOUS CARBONIC SYSTEM IN MINE WATERS AND PRINTS A
 C COMPARATIVE LIST OF SATURATED AND OBSERVED VALUES OF PH,
 C TOTAL ALKALINITY AND CALCIUM CONCENTRATION. AN IMPORTANT
 C FEATURE OF THE CALCULATION IS THE INCLUSION OF A
 C CORRECTION FOR THE EFFECT OF HYDROSTATIC PRESSURE ON THE
 C CARBONIC DISSOCIATION CONSTANTS. THE INPUT PARAMETERS
 C REQUIRED ARE OBSERVED PH, TOTAL ALKALINITY, CALCIUM
 C CONCENTRATION, TEMPERATURE, HYDROSTATIC PRESSURE AND
 C PREVIOUSLY CALCULATED IONIC STRENGTH.

LOEWENTHAL AND MARCHANT MAY 1976

THIS PROGRAM HAS <61 LETTERS PER LINE SO AS TO FIT A4.

DATA INP,10P/8,5/

THIS PROGRAM IS WRITTEN FOR THE UNIVERSITY OF CAPETOWN
UNIVAC 1106.

REAL KI,K2,KW,KS,KIL,K2L,KWL,KSL
 DOUBLE PRECISION Z,ZZ,ALKS,CAS,FRACT
 DIMENSION PHH(100),ALKK(100),CAA(100),UU(100),T(100)
 DIMENSION PR(100),Y2(10),DV(10),DK(10)

SAMPLE DATA ETC. ARE READ IN FROM VARIOUS SOURCES:

C
 C NN IS THE NUMBER OF SAMPLES TO BE READ INTO THE PROGRAM
 C AND MAY NOT EXCEED 100.
 C DV AND DK ARE VOLUME AND DISSOCIATION CONSTANT CORRECTION
 C CONSTANTS FOR HIGH PRESSURE WATERS.
 C T IS TEMPERATURE IN DEGREES CELSIUS, READ IN SITU AT ABOUT
 C ONE ATMOSPHERE PRESSURE.
 C PHH IS SAMPLE PH, MEASURED IN SITU AT ABOUT ONE ATMOSPHERE
 C PRESSURE AND AT AMBIENT TEMPERATURE.
 C CAA IS CALCIUM CONCENTRATION AS MG/L CA++.
 C ALKK IS TOTAL ALKALINITY IN PPM CaCO3.
 C PR IS HYDROSTATIC PRESSURE IN ATMOSPHERES.
 C UU IS IONIC STRENGTH, PREVIOUSLY CALCULATED.
 C LSN IS THE FIRST SAMPLE NUMBER MINUS ONE. (SAMPLE NUMBERS
 C MUST BE CONSECUTIVE INTEGER NUMERICS).

READ(INP,1)NN
 1 FORMAT(I2)
 DO 3 J=1,4
 READ(INP,2)DV(J),DK(J)
 C THESE VALUES, TAKEN FROM REFS. CITED IN APPENDIX 1, ARE:
 C -29.0,0.0,-27.8,-0.0087,-21.0,-0.0052,-58.1 AND -0.0157
 2 FORMAT(2F10.4)
 3 CONTINUE
 DO 5 I=1,NN
 READ(INP,4)T(I),PHH(I),CAA(I)
 4 FORMAT(18X,2F6.0,24X,F6.0,/)

```

      DO 9 I=1,NN
      READ(INP,8)PR(I)
8     FORMAT(F3.0)
9     CONTINUE
      DO 11 I=1,NN
      READ(INP,10)UU(I)
10    FORMAT(33X,F6.4)
11    CONTINUE
      READ(INP,12)LSN
12    FORMAT(I4)
C     LOOPING COUNTERS ARE DEFINED/INITIALISED:
C
C     LML FOR THE MASTER LOOP.
C     L3L FOR THE THIRD ITERATION LOOP.
C     LES FOR THE ERROR ESTIMATION LOOP.
C     LSN FOR TYPING CONSECUTIVE SAMPLE NUMBERS.
C
      LML=0
      LES=0
C     A MASTER LOOP BEGINS WHICH GOVERNS ALL COMPUTATION AND
C     OUTPUT.
      DO 500 I=1,NN
C     FIRST CALCULATED ARE THOSE VALUES WHICH REMAIN CONSTANT
C     WITHIN THE INTERNAL LOOPS.
C     MONOVALENT (FM) AND DIVALENT (FD) ACTIVITY COEFFICIENTS
C     ARE CALCULATED (LOW PRESSURE SYSTEM).
      U=UU(I)
      U1=U**0.5
      F=(U1/(1+U1))-0.2*U
      FD=2*F
      FD=1./((10.**FD))
      FM=0.5*F
      FM=1./((10.**FM))
C     TEMPERATURE IS CONVERTED TO DEGREES KELVIN.
      TA=T(I)+273
C     VALUES FOR THE IDEAL LOW PRESSURE DISSOCIATION CONSTANTS
C     ARE CALCULATED AT THE GIVEN TEMPERATURE, USING STANDARD
C     FORMULAE.
      PK1=(17052./TA)+215.21*ALOG10(TA)-.12675*TA-545.56
      K1=1./10.**PK1
      PK2=(2902.39/TA)+(0.02379*TA)-6.498
      K2=1./10.**PK2
      PKS=(0.01183*T(I))+8.03
      KS=1./10.**PKS
      PKW=(4787.3/TA)+(7.1321*ALOG10(TA))+(0.01037*TA)-
      *22.801
      KW=1./10.**PKW
C     VALUES FOR THE ACTIVE LOW PRESSURE CONSTANTS ARE COMPUTED
C     BY MULTIPLYING THE IDEAL CONSTANTS BY ACTIVITY
C     COEFFICIENTS.
      K1L=K1/FM**2
      K2L=K2/FD
      KWL=KW/FM**2
      KSL=KS/FD**2
C     PRESSURE DEPENDANT RATIO FACTORS ARE GENERATED WHICH WILL
C     BE USED TO CONVERT THE LOW PRESSURE DISSOCIATION
C     CONSTANTS TO HIGH PRESSURE EQUIVALENTS.
      DO 24 J=1,4
      Y=-DV(J)*(PR(I)-1)+0.5*DK(J)*(PR(I)-1)**2.
      Y1=Y/(82.05*TA)
      Y2(J)=EXP(Y1)
24    CONTINUE

```

```

C THE LOW PRESSURE CONSTANTS ARE MULTIPLIED BY THE
C PREVIOUSLY COMPUTED PRESSURE RATIO FACTORS TO GIVE THE
C EQUIVALENT HIGH PRESSURE VALUES FOR THE DISSOCIATION
C CONSTANTS.
  K1=K1L*Y2(1)
  K2=K2L*Y2(2)
  KW=KWL*Y2(3)
  KS=KSL*Y2(4)
C CA++ AS MG/L CA++ IS CONVERTED TO CA++ AS PPM CACO3.
  CAA(I)=CAA(I)/0.400439
C THE CA++ AND ALK DATA, AS PPM CACO3, ARE CONVERTED TO
C (EQUIVALENT) MOLES PER LITRE.
  CA=CAA(I)/10.**5.
  ALK=ALKK(I)/(5.*10.**4.)
C THE CONSERVATIVE PARAMETER ALK-2CA++ WILL BE NEEDED LATER
C IN THE ITERATION LOOPS.
  Z=ALK-2*CA
C THIS COMPLETES THE CALCULATION OF VALUES EXTERNAL TO THE
C LOOPS. THE INNER LOOPS NOW BEGIN WITH CALCULATION OF
C VALUES FOR THE LOW PRESSURE SYSTEM.
C LOW PRESSURE ACIDITY IS COMPUTED IN SEVERAL STEPS.
  30 PH=PHH(I)
  H=(1./10.**PH)/FM
  OH=KW/H
  HCO3=(ALK-OH+H)/(2*K2L/H+1.)
  ACID=2*H*HCO3/K1L+HCO3+H-OH
C THIS COMPLETES THE LOW PRESSURE CALCULATIONS.
C COMPUTATION OF HIGH PRESSURE DATA NOW BEGINS.
C SOLVE FOR H AND THUS HIGH PRESSURE 'OBSERVED' PH (PHP).
  A=ACID-(2.*K2)-ALK
  B=A**2
  C=(2.*ALK)/K1+1.
  D=4.*C+2.*K2*ACID
  E=(B+D)**0.5
  HP=(A+E)/(2.*C)
  PHP=(-1.)*ALOG10(FM*HP)
C THE ITERATION FOR SOLVING FOR HIGH PRESSURE SATURATED
C VALUES FOR PH, ALK AND CA++ BEGINS.
C L3L IS A LOOPING COUNTER FOR THE ITERATION.
  L3L=1
C 'OBSERVED' HIGH PRESSURE PH IS TAKEN AS THE FIRST
C APPROXIMATION TO THE HIGH PRESSURE SATURATED PH.
  PHS=PHP
C THE FIRST LOOP BEGINS. IT ENSURES THAT THE FIRST
C APPROXIMATED PH VALUE IS ABOUT 0.1 TOO LOW, I.E., HIGH
C VALUES ARE ELIMINATED.
  35 HS=(1./10.**PHS)/FM
  OHS=KW/HS
  HCO3=(ACID-HS+OHS)/(2*HS/K1+1)
  ALKS=2*K2*HCO3/HS+HCO3+OHS-HS
  CO3S=K2*HCO3/HS
  CAS=KS/CO3S
C AN APPROXIMATION TO THE SATURATED VALUE OF ALK-2CA++ IS
C MADE.
  ZZ=ALKS-2*CAS
C THE TWO VALUES ZZ AND Z ARE COMPARED FOR FIT. WHEN THIS IS
C GOOD ENOUGH, CONTROL PASSES TO THE SECOND LOOP.
  IF(ZZ-Z)50,60,40
  40 PHS=PHS-0.1
  GO TO 35
C FRACT WILL ALLOW THE LOOP TO PROGRESSIVELY IMPROVE THE
C APPROXIMATED PH VALUE BY ONE DECIMAL PLACE AT A TIME.

```

```

50 FRACT=0.01
C THE SECOND LOOP BEGINS. IN CONJUNCTION WITH LOOP 3, IT
C WILL IMPROVE THE 'FIT' OF THE PH VALUE ONE DECIMAL AT A
C TIME.
55 PHS=PHS+FRACT
HS=(1./10.**PHS)/FM
OHS=KW/HS
HCO3=(ACID-HS+OHS)/(2*HS/K1+1)
CO3S=K2*HCO3/HS
ALKS=2*CO3S+HCO3+OHS-HS
CAS=KS/CO3S
C THE VALUE OF ZZ-Z IS NOW TESTED FOR A GIVEN VALUE OF
C FRACT. THE CORRESPONDING APPROXIMATED PH VALUE IS EITHER
C RETURNED THROUGH THE LOOP FOR IMPROVEMENT, OR ELSE CONTROL
C PASSES TO LOOP 3, WHERE FRACT IS LOWERED, AND THENCE BACK
C THROUGH LOOP 2 ONCE AGAIN.
ZZ=ALKS-2*CAS
IF(ZZ-Z)55,60,60
C THE THIRD LOOP BEGINS. IT COUNTS THE NUMBER OF DECIMALS IN
C FRACT, ENSURES THAT THE APPROXIMATED VALUE OF PH IS ALWAYS
C A BIT TOO LOW AND REDUCES FRACT STEPWISE WITH EACH PASS.
60 L3L=L3L+1
PHS=PHS-FRACT
FRACT=0.1*FRACT
C WHEN THE PRECISION OF THE APPROXIMATED PH IS GOOD TO SIX
C DECIMALS, THE NESTED LOOPS 2 + 3 OPEN. THUS THE ITERATION
C ENDS AND THE HIGH PRESSURE CALCULATIONS ARE COMPLETED.
IF(L3L-6)55,55,100
C
C THE LAST SECTION OF THE PROGRAM CALCULATES VARIOUS
C DIFFERENCES AND CONVERTS THEM, WHERE NECESSARY, INTO PPM
C CALCIUM CARBONATE, ALTERNATELY REDIRECTS CONTROL BACK INTO
C THE MASTER LOOP TO COMPUTE ESTIMATED ERROR IN (SATURATED
C CA++ - OBSERVED CA++) AND SELECTS APPROPRIATE WRITE
C COMMANDS FOR DIFFERENT LOOP CYCLES.
C
C DCA IS THE DIFFERENCE BETWEEN THE SATURATED AND OBSERVED
C VALUES OF CA++.
100 DCA=CAS-CA
C CONVERT DCA INTO PPM CACO3, DROPPING DECIMALS.
IDCA=IFIX(DCA*10**5)
C TEST IF THE ERROR STEP HAS BEEN COMPLETED.
IF(LES-1)200,400,400
C PHD IS THE DIFFERENCE BETWEEN LOW AND HIGH PRESSURE PH
C VALUES.
200 PHD=PHH(1)-PHP
C CONVERT CAS AND ALKS TO PPM CACO3, DROPPING DECIMALS.
ICAS=IFIX(CAS*10**5)
IALKS=IFIX(ALKS*5*10**4)
C THE DECIMAL PORTIONS OF CERTAIN OBSERVED VALUES ARE
C DROPPED.
IALK=IFIX(ALKK(1))
ICAA=IFIX(CAA(1))
C THE SAMPLE NUMBER COUNTER IS INCREMENTED.
LSN=LSN+1
C TESTING LML ENABLES THE MASTER LOOP TO JUMP THE TITLE
C OUTPUT COMMAND AFTER THE FIRST CYCLE.
LML=LML+1
IF(LML-1)300,300,310
C TITLES ARE WRITTEN.
300 WRITE(IOP,305)
C INSERT REQUIRED TABLE NUMBER IN THE FOLLOWING LINE.

```

```

305 FORMAT(1H1,42X,'TABLE 4.5',//,
*21X,'VALUES OF IMPORTANT OBSERVED AND SATURATED CARBO'
*, 'NIC SYSTEM',/,
*34X,'PARAMETERS IN TSUMEB MINE WATERS',////,
*43X,'ALL IN P.P.M. CALCIUM CARBONATE',/,
*43X,'*',29X,'*',/,
*26X,'OBS OBS LP * SAT EST *'
*,/,
*21X,'SPL LP HP -HP *OBS OBS SAT -OBS ERR '
*, 'SAT* SAT',/,
*21X,'NO. PH PH *ALK CA CA CA CA '
*, 'ALK* PH',/,
*21X,'*****')
C SELECTED OBSERVED AND CALCULATED VALUES ARE WRITTEN.
310 WRITE(10P,315)LSN,PHH(I),PHP,PHD,IALK,ICAA,ICAS,IDCA.
*IALKS,PHS
315 FORMAT(1H ,20X,13,2X,F4.2,2X,F4.2,2X,F4.2,2X,13,2X,13,
*2X,13,2X,14,7X,13,2X,F4.2)
C THE ERROR CALCULATION LOOP COUNTER IS INCREMENTED.
LES=LES+1
C THE UNCERTAINTY OF PH MEASUREMENT (0.05) IS SUBTRACTED
C FROM OBSERVED PH AND THE VALUE RETURNED TO THE ITERATION
C LOOPS FOR THE CALCULATION OF A CORRESPONDING UNCERTAINTY
C IN THE VALUE OF SATURATED CA++.
PHH(I)=PHH(I)-0.05
C THE VALUE OF IDCA IS PRESERVED PRIOR TO IDCA BEING
C OVERWRITTEN BY THE ERROR CALCULATION LOOP.
IDDCA=IDCA
GO TO 30
C THE ERROR LOOP CONTROL COUNTER IS RESET.
400 LES=0
C THE (ABSOLUTE) DIFFERENCE BETWEEN THE TWO VALUES OF IDCA
C IS THE VALUE OF THE UNCERTAINTY IN THE VALUE OF SATURATED
C CALCIUM CONCENTRATION.
ID2CA=IABS(IDCA-IDDCA)
C THE VALUE OF THE ERROR IN (SATURATED CA++ - OBSERVED CA++)
C IS WRITTEN ON THE SAME LINE AS THE OTHER OUTPUT DATA.
WRITE(10P,410)ID2CA
410 FORMAT(1H+,64X,13)
C THE MASTER LOOP CLOSSES.
500 CONTINUE
C FOOTNOTES ARE WRITTEN BELOW THE OUTPUT TABLE OF RESULTS.
WRITE(10P,600)
600 FORMAT(1H0,21X,'NOTE: ABBREVIATIONS USED ARE (FROM LE'
*, 'FT TO RIGHT), SAMPLE',/,
*28X,'NUMBER, OBSERVED, LOW OR HIGH PRESSURE, ALKALINI'
*, 'TY',/,
*30X,'CALCIUM CONCENTRATION, SATURATED, AND ESTIMATED',
*,/,
*33X,'ERROR (IN THE VALUE OF (SAT - OBS)CA++).'')
STOP
END

```


APPENDIX J

Miscellaneous experiments aimed at monitoring the quality of data collected during the orientation survey of borehole waters in the Otavi Mountainland

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APPENDIX J

Miscellaneous experiments aimed at monitoring the quality of data collected during the orientation survey of borehole waters in the Otavi Mountainland

J1. CHANGES IN THE COMPOSITION OF STAGNANT BOREHOLE WATER DURING THE FIRST HOUR OR FEW HOURS OF RENEWED PUMPING

J1.1 Introduction

Two important, interdependent questions arise in the study of borehole waters during hydrogeochemical exploration: (a) to what extent does the pumping equipment contaminate the sample? (b) how long must the equipment operate before a representative sample of water can be obtained?

It is intuitively reasonable to suppose that one could contribute to the understanding of these issues by studying the compositions of stagnant waters that had been in contact with the well-fittings for some time and, in particular, by noting the changes in the composition of the flow from the pump when it is restarted after a longish period of disuse. Oddly enough, the literature contains extremely few descriptions of experiments of this kind. The idea of an investigation of this kind was first suggested to the writer by Webb (pers. comm.) in 1972. Edmunds (1973 /983/) conducted an analogous experiment at Spalding in the United Kingdom. He found no serious contamination of water flowing from artesian boreholes that had been sealed for many months.

What is true at Spalding is not necessarily true in the Otavi Mountainland, and a search was therefore made in the Tsumeb area for boreholes that could be used in a local experiment of this nature. Two conditions had to be met: (i) The borehole must have been idle for an uninterrupted period of at least one week and preferably much longer. (ii) The borehole must have been a known source of metalliferous water - there is little point in trying to detect metal contamination in a metal free sample.

These conditions are not easy to meet simultaneously, but fortune nevertheless provided four boreholes that were eminently suitable for the purposes of the planned experiment. The pumps in these boreholes were restarted and water samples were collected from them at regular intervals for up to one hour or, in the case of one particular hole, four hours. All the standard precautions were observed during sampling (Chapter 5) and the analytical methods used were those described in Appendix B (especially B4.2 and B4.5).

Note particularly that (i) the suspended metals and the dissolved metals were determined in two separate one litre samples collected within seconds of each other. (ii) the suspended metals were separated by filtration of an unacidified aliquot. (iii) the "dissolved" metals were determined by solvent extraction (APCD/MIBK) of an unfiltered, acidified aliquot (10 ml HClO_4 per litre). Thus the value for the "dissolved" metal is the sum of the amount of metal that was present naturally in solution plus the amount leached from the suspended fraction by the preserving acid and/or the analytical reagents.

The samples were randomized before analysis. The principle results of this pumping experiment are compiled in Table J1(1). Precision data for this series of analyses are given in Table J1(2).

J1.2 Interpretation

(A) MAJOR COMPONENTS AND ELECTRODE MEASUREMENTS

The same broad patterns were observed in the available data for all four holes. The sodium and potassium values are probably a fairly good "index" to the state of the major component composition of the waters. It appears that the concentrations of the major components had, in all observed cases, stabilized within five minutes of the commencement of pumping. The millivolt readings tended to increase as "reduced", probably oxygen-poor water was cleared from the hole. The Notweide flow exhibited a downward "loop" in mV readings between one and fifteen minutes elapsed, probably because of stratification in the column of water being pumped out. The mV readings always reached a fairly stable level within fifteen minutes, even in the case of the flow from the relatively slow-yielding Kranzberg pump. The pH readings decreased and became stable within fifteen minutes. Radical changes in Eh/pH conditions were noticeable only in the first waters disembogued from the two boreholes that had stood idle for many months.

(B) DISSOLVED AND SUSPENDED TRACE METALS

Consider first the Welcome and Notweide boreholes, which are fitted with rotary (centrifugal) force pumps. i.e., devices in which power is transmitted from the surface to a submerged pump unit via a rotating shaft. Pumps of this type have a relatively high yield. At the time of the experiment neither pump had been continuously idle for longer than a month.

EXPLANATION OF TABLE J(1)1

- * The initial sample collected at Bobos House (0:00:00) was sludge and was discarded.
- ** Some samples have very low values for TSS and therefore a high relative experimental error is probable in the calculation of the proportion of metals present. For TSS values below 1 mg/l the concentrations of metals are given as the probable range of the actual value, assuming a error of mass of 0,8 mg.
- *** Values in parentheses are for unacidified samples collected at the same time.

Samples 37a and 37b are check samples collected within a period of about one minute.

The mV readings are relative to an Fe(II)/Fe(III) standard at 27⁰ C (Appendix B).

Welcome Post borehole and those at Notweide and Bobos House fitted with high-yield rotary pumps. Kranzberg East borehole fitted with low-yield reciprocatory pump.

Periods of inactivity prior to renewed pumping are: Welcome post 3-4 weeks; Notweide 10-20 days; Bobos House 12 months; Kranzberg East several months.

TABLE J1 (2)

VALUES FOR MULTIPLE ANALYSES OF SAMPLES COLLECTED DURING THE STUDY OF OLD BOREHOLE WATERS

(A) Copper lead and zinc ($\mu\text{g/l}$)

Sample	Cu	Pb	Zn
1	-	-	71-78
2	6-5	<1-<1	155-215
3	1-2	1-2	-
4	5-5	<1-<1	7-4-7-8
5	13-32	2-2	-
6	-	-	34-31
7	6-3	<1-<1	-
8	19-41	80-80	-
9	-	-	157-183
10	-	-	48-48
11	<1-<1	7-6	-
12	1-<1	3-7	850-1230
13	49-29	82-90	4760-4580
14	-	-	10200-10140
15	-	-	358-278
16	-	-	48-295

(B) Comparison of data ($\mu\text{g/l}$) for determination of zinc by two methods

Sample	Direct AAS	MIBK extraction AAS
1	25	26
2	148	148

(C) mV readings

Sample	mV
1	286-180
2	308-340
3	317-335
4	321-344
5	359-368

mV readings relative to an Fe(II)/Fe(III) standard at 27⁰ C, giving the following precision data:

$$\bar{x} = 428 \quad n = 8 \quad \sigma = 6,4$$

Ignore for the moment the data for the first few minutes. After five minutes of pumping, each pump was delivering clean water in which the pH was nearly neutral, the mV reading was moderately or strongly positive and the load of suspended solids was very low. These waters had extremely low concentrations of dissolved and suspended copper and lead. Therefore these pumps were not adding ponderable amounts of these two metals to the flow of water at that stage. In each of the abovementioned clean samples the concentration of dissolved zinc exceeded one milligram per litre and in one case it was more than 5 mg/l. At the same time the amount of suspended zinc never exceeded 180 $\mu\text{g/l}$ and in most cases it was below 10 $\mu\text{g/l}$. One expects that an operating rotary pump would shed metal mainly in the form of small flakes, rather than as ions. It is difficult to believe that a rotary pump could have continuously shed from 1 to 5 mg/l of dissolved zinc to the flow while supplying a mass of suspended zinc that was two or three orders of magnitude smaller. One must conclude that the great bulk of the dissolved zinc was not a contaminant but was a natural constituent of these waters, which were therefore genuinely anomalous. Note that there were significant fluctuations in the natural concentration of zinc.

If one returns to the data for the first 3-5 minutes it will be noted that most samples had relatively elevated concentrations of copper, lead and zinc in suspension. There are three important feasible sources (which need not be mutually exclusive) for a concentration of suspended metals such as this:

(1) The high initial concentrations may have been caused by an exceptionally rapid rate of wear of the machinery during the first minutes of operation, because of the presence of oxidic films on the moving parts, or small sand grains, or some similar phenomenon. It appears that this was not the dominant mechanism, for two reasons: (a) the proportions of copper, lead and zinc (columns 15 to 17) in the suspended matter from the Notweide flow (there is insufficient data for the Welcome flow) did not decrease consistently with time. (b) the peak output of zinc in the Notweide flow occurred after the peak outputs of copper and lead. It is hard to see why the zinc-rich parts of a pump should suffer an acute attack of friction a full minute after the copper- and lead-rich parts had had theirs.

(2) The naturally-occurring solids (e.g. organic matter) in the borehole may have absorbed and accumulated metal ions released by corrosion of the metallic parts of the well fittings. It is well known /920/ that organic matter has a marked affinity for many metallic ions and can absorb appreciable masses of them from natural water. However, it appears that this could not have been the dominant process. Much more copper than lead is used in the construction of a borehole pump and one would therefore

expect that copper would have been more abundant than lead in the solids that accumulated nearby; but in fact the amount of suspended lead in the earliest samples from the Notweide and Welcome suites was similar to and sometimes greater than the corresponding amount of copper. In the case of the early Bobos flow (0-6 minutes) both the absolute mass and relative proportion of lead were so high that it is very difficult to imagine that the pump itself could have been the source of the metal. There is of course no need to look to the well fittings as a source of zinc because it occurred naturally in large amounts in solution.

(3) It is therefore likely that a large part of the mass of suspended metal originally existed naturally in solution and was captured by the solids in or near the borehole.

Note that the concentrations of copper and lead in suspension frequently exceeded the corresponding concentrations of these metals in solution. This shows that these metals are quite strongly bonded to the suspended phases and are not readily leached out of them by the dilute perchloric acid used as a preservative.

Consider now the data for the Bobos borehole. This hole is different from the Welcome and Notweide holes in several respects: (a) It was drilled only a few metres from a small, oxidized Cu-Pb-Zn-V orebody. Water samples drawn from this borehole will almost certainly be anomalous; indeed the reason that it had not been used for a year was that the metal content of the water constituted a health hazard. (b) Because the pump had not been used for 12 months, at least part of the column of water in it had experienced an increase in pH and a decrease in redox potential. These changes are known to promote the precipitation of many heavy metals /49/, especially lead, which is generally the least mobile of the trio Cu-Pb-Zn. (c) The Bobos borehole appeared to have large, if variable, reserves of suspended solids. After 75 minutes the load of total suspended solids (TSS) was still two-thirds of what it was at 1-3 minutes, whereas even the slow Kranzberg pump was delivering water 90% cleaner at the end of the first hour. Casual observation suggested that the suspended matter from the Bobos flow was largely organic. Nevertheless, the composition of this suspended material was not uniform. It was much richer in metals in the early phases of the experiment and gradually became less metalliferous in the later stages, except for a pronounced "surge" in the concentrations of all three metals after 50 minutes had elapsed. Note that the proportion of metals in the suspended solids dropped sharply at the same time that the pH dropped to 7.0 and the millivolt readings first exceeded +250.

One may attribute the high mass of suspended metals to several factors: (i) the close proximity of ore. (ii) the prolonged period of inactivity, which allowed the development, in certain parts of the column

of water adjacent to the borehole, of Eh-pH conditions favourable to the immobilization of metals (especially copper and lead). (iii) an abnormally high TSS load. This may also be related to factor (ii) *supra*.

It appears to be impossible, without further information, to decide the relative importances of these different influences. Note that despite the high absolute masses of copper, lead and zinc the proportions of these metals in the TSS load were not particularly weighty (cols.15-17). It is not possible to label the Bobos waters anomalous on the basis of a comparison of the data in these columns with the corresponding data for the Notweide and Welcome boreholes. Nevertheless the Bobos waters *are* anomalous; this is shown by the fact that the concentrations of dissolved metals, especially lead, remained notably high even though (a) the corresponding values for suspended metals dropped to relatively low levels and (b) the suspended metals are probably poorly soluble.

Note that the amounts of dissolved metals fluctuated considerably with time. This was especially true of zinc, which showed a sharp decrease in concentration at the same time that the amount of suspended zinc decreased suddenly. There are two important possible explanations for this phenomenon: (a) The release of zinc ions, as a result of corrosion, becomes a significant factor over a period of many months. (b) The still waters at the bottom of the borehole become equilibrated with respect to the metalliferous suspendable solids and are thereby also enriched in zinc.

The Kranzberg hole is the only one of the four boreholes that is fitted with a reciprocating pump; i.e., one in which the rods move up and down within the casing. The rods had been broken for several months and the task of dismantling, repairing and reassembling them had been completed only minutes before the first water samples were collected. There are some similarities between the data for the Bobos and Kranzberg holes. Both pumps stood idle for many months and both yielded dissolved and suspended metals much more abundantly than the "cleaner" Notweide and Welcome boreholes. Nevertheless, there are some important differences, which suggest that the flow from the Kranzberg borehole was significantly contaminated.

There is no doubt that overwhelming quantities of metallic zinc were added to the samples. Tiny, coruscant flakes of metal - probably rubbed from galvanized coatings - were still clearly visible in the stream from this pump after four hours of operation. Although the rate of wear had decreased dramatically by this time, the concentration of suspended zinc still exceeded 8 mg/l. Since the TSS load also decreased with time - as it did in all the boreholes studied - the proportion of zinc in the suspended

solids remained immoderate throughout the experiment; approximately one-third of the solids was elemental zinc. These fragments of zinc were not readily dissolved by the perchloric acid added, but some attack did occur (samples 36 and 37a) and this added at least 4 mg of zinc per litre to the dissolved constituents of this pair of samples. Something like 90% of the zinc that was present in the dissolved state in these samples when they were analyzed was released into solution by the action of the acid upon the suspended solids.

The question of the degree of contamination by copper and lead is more problematical. The distributions of the concentrations of these metals in suspension and solution (cols. 4-9) in the Kranzberg samples was not unlike the corresponding distribution for the Bobos samples. However, the data in columns 15 and 16 show a reversed trend that may well indicate that the Kranzberg waters were contaminated. Despite the fact that the data for zinc suggest that the rate of wear of metallic components decreased rapidly with time, the proportion of copper in the TSS load, like the corresponding proportion of zinc, did not show any systematic decrease with time - if anything, the contrary was true - while the proportion of lead showed a definite, smooth rise during the four-hour period.

If particles of a given metal were being worn from exposed surfaces at a constant rate, then the proportion of the metal in the TSS load would have risen as the total amount of non-metallic solids (carbonates, organic matter etc.) decreased as the flow became progressively cleaner with passing time. This model can remain valid for a decreasing rate of wear also, provided that the "decay constant" for the wear curve exceeds that of the TSS curve. There is a good possibility, therefore, that the unique features of the Kranzberg data in columns 15-17 are a sign of contamination by metallic particles. It is difficult otherwise to explain why these data represent a reversal of the generally observed rule that the proportion of metals in the suspended fraction decreased with time. There is nothing to suggest that this borehole is drilled near ore. Geophysical surveys in the immediate vicinity of the hole revealed nothing of interest /30/ and lithochemical analysis of material from the borehole core showed only background concentrations of copper, lead and zinc /189/ (Table J1(3)).

The Kranzberg pump, which usually runs for only a few hours a week, may continue to contaminate the flow of water for months or years, until that stage is reached where most of the galvanizing etc. has been rubbed off the exposed surfaces of the rods, casings and other parts. It follows that reciprocating pumps are to be avoided in hydrogeochemical surveys in which "total" metals (i.e. dissolved and acid-soluble metals) are to be determined. Fortunately this type of pump is rare in the Tsumeb and adjacent

TABLE J1(3)

ANALYSES OF COMPOSITE CHIP SAMPLES FROM THE KRANZBERG EAST BOREHOLE

sample	Cu	Pb	Zn
1	9	46	35
2	5	34	24
3	6	34	26
4	5	35	20
5	7	34	26

Sample 1 is from the lower end of the core and sample 5 from the upper end.

The analytical method (AAS) is described in reference /189/.

districts, where the more efficient rotary pump is more popular.

J1.3 Conclusions

(1) Experiments of this sort are rarely reported and so it is difficult to measure the implications thereof against the yardstick of other people's results. It is obvious that this kind of research may be able to tell us a great deal about the nature of the metal content of the suspended and dissolved loads in borehole water, and about the degree and nature of metallic contamination from borehole hardware. With hindsight, it is easy to see that some important modifications could profitably be made to the experimental method - examples are the inclusion of additional, non-anomalous boreholes and the division of all samples into filtered and unfiltered aliquots. It was, regrettably, not possible to repeat the experiment during the field work for this thesis.

Despite the lack of inopprobrious conclusions about some of the observed phenomena, other observations are indeed pertinent to the orientation study (Chapter 5) and should be noted:

(2) The data indicate that rotary pumps are not sources of unmanageable contamination. Reciprocating pumps must, however, be viewed with a sceptical eye.

(3) Boreholes that have been pumped regularly - particularly in the weeks preceding sampling - will probably yield a useful water sample within 10-15 minutes of renewed pumping. Boreholes that have been idle for months, or which continuously yield large amounts of suspended solids, ought to be regarded as special cases. Fortunately these were very rare in the area studied.

(4) Provided that the aforementioned conditions are met, there appears to be no intrinsic objection to the "total metal" method, in which the unfiltered sample is acidified. If the water is anomalous the solids will probably also be so and the partial dissolution of the suspended phase will serve to enhance the anomaly in the solution.

(5) There does not appear to be any simple method of telling, from a single sample, whether a metal "anomaly" in borehole water is due to contamination or to mineralization. This is not a serious problem, because the number of spurious anomalies will probably be small, and steps can be taken later to eliminate them. To attempt to do so during routine sampling operations would be a serious waste of time. (Later events in this study appeared to corroborate these conclusions. The number of anomalies detected during the application phase (Chapter 6) was remarkably small, which could not have

been the case had there been serious contamination from the metallic components of the borehole hardware and pumps that provided the samples.

J2. MONITORING OF TRACE ELEMENT CONTAMINATION FROM THE WALLS OF SAMPLE CONTAINERS

It is obviously essential to know how much metal is added to the sample by the container in which it is stored. The containers used in this thesis project have been intensively studied from this point of view and much of the data obtained by the writer and co-workers has already been presented in reports, theses and published papers /1001-4/. More than a dozen elements were studied by several techniques, including the use of radioisotopes and low temperature radio-frequency ashing, but there was no evidence of any significant contamination.

The additional data presented here were collected from tests done by the writer in the field, rather than under the more favourable conditions prevailing in the laboratory, and have not previously been published. These additional tests involved the most important metallic pathfinders (copper, lead and zinc) and also sodium. Two types of plastic containers were tested in triplicate:

- (i) The one litre HDPE bottles with unlined, press-fit HDPE closures used in the study of the Tsumeb mine waters and in the orientation study of the borehole waters of the Otavi Mountainland.
- (ii) A similar type of one litre HDPE container that was used in addition to those mentioned in (i) during sampling in the Withdrawal area (Chapter 6). This type of bottle has a screw-on PVC lid that is lined with plastic and were used when supplies of the other type of bottle were exhausted. Both types were supplied by Consolidated Glass Ltd., in Johannesburg.

The blank fluid was pure water (Appendix B). The bottles were cleaned by soaking them in dilute acid and rinsing thoroughly with pure water. They were then filled to a reference line (800 ml) and 20 ml of HClO_4 was added from the same autodispenser used for all the samples collected routinely (e.g. Chapter 5). The bottles were closed and shaken. The samples were then frozen at minus twenty degrees Celsius for a week, thawed, and analysed for Cu, Pb, Zn and Na by the methods described in Appendix B. The results of these determinations are compiled in Table J2.

There is clearly no problem with copper, lead and sodium. The samples stored in the bottles with unlined lids (1 to 3) were less contaminated with zinc than those kept in bottles with lined lids (4 to 6). It has often been observed that the liners of lids are an important source of contamination of water samples /209,1002/. Allowance must be made in both cases for the

TABLE J2

RESULTS OF ANALYSES OF CONTAMINATION TEST SAMPLES AND BLANKS

Sample	Cu $\mu\text{g/l}$	Pb $\mu\text{g/l}$	Zn $\mu\text{g/l}$	Na mg/l
1	<1	<1	9	0
2	<1	<1	5	0
3	<1	<1	6	0
4	<1	<1	10	0
5	<1	<1	11	0
6	<1	<1	21	0
6a	-	-	21	0

Sample 6a is a duplicate analysis of sample 6

None of the four metals was detectable in any sample of blank fluid.

Samples 1 to 3 were stored in containers with unlined lids.

Samples 4 to 6 were stored in containers with lined lids.

zinc contributed by the perchloric acid. According to the guaranteed specifications provided by the manufacturers, this will amount to between 0 and 10 $\mu\text{g Zn per litre}$. In any event, no more than 11 to 21 $\mu\text{g/l}$ of zinc was contributed by the containers to the fluid in them. This is negligible when compared to the concentrations of zinc found in natural samples collected during the second orientation and application studies (Section III). The mass of zinc derived from the containers was of the order of only 1% of the total amount of zinc present in the most anomalous samples from the Withdrawal area.

J3. STABILITY OF UNACIDIFIED SAMPLES USED FOR THE DETERMINATION OF MAJOR COMPONENTS

A bulk sample was collected from borehole number 288 (Vegetable Garden east-central hole) on 1975-05-13 and analyzed for major components thirteen times in the following eleven days. Table J3 gives the results, in the units in which they were reported, together with mean values and standard deviations. The reproducibility is very good and the samples did not deteriorate significantly during the eleven day period.

Almost all of the major element determinations recorded in this thesis were made on the day that the samples were collected. The longest delay, in the case of a handful of samples submitted for re-analysis, was 48 hours. It is therefore clear that the quality of the data was not diminished by changes in the bulk compositions of the samples that were awaiting analysis.

J4. ESTIMATION OF THE NATURAL SEASONAL DRIFT IN THE COMPOSITIONS OF BOREHOLE WATERS AS A RESULT OF METEOROLOGICAL AND RELATED FACTORS

J4.1 Methods

The identification of the characteristics and magnitudes of groundwater anomalies and attempts to use this information for purposes of prospecting would be bootless were these features vagarious and transient. Similarly, a vagulous background value would seriously limit the confidence with which any anomaly could be identified. It is for this reason that studies of seasonal variations in the compositions of groundwaters are commonly annexed to hydrogeochemical exploration programs (e.g. /910,991,1110/). It is very difficult to make theoretical predictions about cyclic seasonal changes in the composition of the groundwaters of the Tsumeb area because so little is known about local rates of penetration of precipitation,

TABLE J3

THIRTEEN ANALYSES OF A SINGLE BULK SAMPLE OVER A PERIOD OF ELEVEN DAYS

Date	TH	CaH	MgH	NaCl	PA	MA	SO ₄ ⁼	pH
1975 May 13th	756	364	392	220	nil	445	211	7,0
13	756	364	392	220	nil	445	259	7,0
14	756	364	392	220	nil	445	230	7,0
14	756	364	392	220	nil	445	228	7,0
15	756	364	392	220	nil	445	219	7,2
16	756	364	392	220	nil	445	214	7,6
17	760	364	396	220	nil	445	217	7,1
18	760	364	396	220	nil	445	213	7,1
20	768	360	408	220	nil	445	215	7,2
21	764	360	404	220	nil	445	214	7,2
22	768	360	408	220	nil	445	211	7,4
23	768	360	408	220	nil	445	216	7,2
24	764	360	404	220	nil	445	217	7,1
\bar{x}	760,6	362,5	398,2	220	nil	445	220,3	7,16
σ	5,12	1,93	7,05	0	0	0	12,72	0,16

TH is total hardness, mg/l CaCO₃

CaH is calcium hardness, mg/l CaCO₃

MgH is magnesium hardness, mg/l CaCO₃

NaCl is chloride as mg/l NaCl

PA is P alkalinity, mg/l CaCO₃

MA is M alkalinity, mg/l CaCO₃

SO₄⁼ is sulphate as SO₄⁼

See Appendix B for additional information about these measurements and for methods of analysis.

degree of recharge, speed of re-equilibration of the composition of the groundwater, volume of lateral outflow etc. (see Appendix H). The problem can be tackled only empirically. Useful experimental information was available from records kept by the Department of Water Affairs (DWA) /270/ and from the writer's own studies.

An examination was made of several thousand analyses of waters from scores of groundwater sources, which are on file at DWA. It is not possible to reproduce any of this data here. These analyses span the period from about 1966 to 1974. In many cases it was possible to correlate some of these results with the results that were obtained for samples collected by the writer in 1974-5. This comparison showed clearly that the major features of the hydrological regime had not altered greatly in the preceding five years. In many cases the concentrations of many components in the waters of particular boreholes remained remarkably constant over a period of several years. Exceptions could naturally be found, in which pronounced differences were recorded from one year to the next, but these were not common.

The writer resampled various boreholes in the Tsumeb area on several occasions during a period of over a year. In studying seasonal changes in composition it is obviously necessary to pay particular attention to the precision of analysis. This was done by submitting undeclared duplicate samples with each batch of waters collected during each resampling event. Table J(4)1 is an example of the precision data generated during a typical event. One particular borehole - the Vegetable Garden east-central hole, number 288 - was sampled at intervals of about one week for several months. The results are given in Table J(4)2. The composition of the water remained remarkably constant.

A number of other boreholes in the Tsumeb area were resampled at less frequent intervals. These test holes included the most heavily pumped sources of groundwater in the district (excepting the mines themselves). It is improbable that any farm borehole would have a monthly yield anything like, say, the New Lucerne borehole or the Vegetable Garden boreholes (Table J(4)4. The set of test boreholes is therefore likely to provide some indication of the maximum change due to heavy extraction of water from a point source. The data collected during the resampling experiments are compiled in Table J4(3).

It is difficult to apply formal statistics meaningfully to results of this kind; the significance of the statistical parameters are related in too subjective a manner to the type of analytical measurement, its intended use and the level of concentration at which the determination was made. For example, a coefficient of variation of 100% in a seasonal series of sulphate determinations at a mean concentration of 100 mg/l would be disastrous,

but at a level of 2 mg/l it would be trivial. It proved to be more convenient to assess the data by constructing a semi-quantitative "rank" table (Table J(4)4). The observed differences in composition from one sampling event to the next were consigned to one of three classes:

Class N: The observed differences are negligible. They would not seriously influence the interpretation of the exploration data nor the identification of anomalies.

Class M: The observed differences between sampling events are moderate. They are too great to be dismissed as trivial but are nevertheless unlikely to affect one's assessment of whether or not the water is anomalous.

Class S: The differences are severe and are likely to affect one's assessment of the hydrogeochemical character and significance of the samples drawn from the borehole at different times. If the element so affected were a pathfinder, there would be a good possibility of misjudging the potential importance of the sample.

The boundaries of these three classes are naturally fuzzy and no attempt was made to quantify them.

It can be seen from the column summary in the table that the seasonal stabilities of $[SO_4^{=}]$, $[Cl^-]$, M alkalinity, P alkalinity, [Cu], [Pb] and [Na] are very good, while the stability of [Zn] and total hardness is fairly good. This is fortunate, because sulphate, copper, lead and zinc are important pathfinders in the study area (Section III). Calcium hardness, magnesium hardness, [TDS] and pH are moderately to poorly stable. This is really of little consequence, since none of these parameters is known to be of much use in hydrogeochemical exploration in the Tsumeb area.

Adding all the S scores for each borehole, one finds that 16 of them have either zero, one or two s-values, which are almost always due to shifts in the values of hardness or pH. Only one borehole, the New Lucerne hole, showed a serious overall change in chemical composition, with five S-scores. Despite this, the changes in the concentrations of sulphate and chloride are only moderate. It is probable that the New Lucerne hole is the most heavily pumped of all local boreholes. It is also the hole most likely to be influenced by recycling of water from the nearby slimes dam (Section II and Appendix H). The water from the New Lucerne borehole has a rather low chloride/sulphate ratio and a very high concentration of sodium, which tempts one to compare it with the waters of the Tsumeb mine (Chapter 4). However, there is no obvious connection between this water and any of the major types of mine waters.

Thus it may be said that the gross changes observed in the water at the New Lucerne site are unlikely to be typical of the changes that are to be expected in the average, small borehole used for watering stock.

J4.2 Conclusions

The seasonal variations in the composition of water from a typical borehole in the Tsumeb district is small and the rate of change is slow. Since all individual sampling programs (orientation or application) were completed within a few days or weeks, it seems very unlikely that seasonal drift could be a serious obstacle to hydrogeochemical interpretation in the vicinity of Tsumeb and the Otavi Mountainland.

TABLE J4(1)

DUPLICATE ANALYSES OF THREE CHECK SAMPLES SUBMITTED DURING RESAMPLING TO
DETERMINE SEASONAL DRIFT (MARCH 1975)

sample	assay	PA	MA	pH	Cl ⁻	SO ₄ ⁼	TDS	TH	CaH	MgH
1	1	nil	470	7,2	20	17	420	465	180	285
1	2	nil	464	7,2	30	14	432	460	195	265
2	1	nil	398	7,1	260	252	1084	760	300	460
2	2	nil	406	7,2	250	252	1192	765	285	480
3	1	nil	386	7,0	525	442	1508	805	310	495
3	2	nil	383	7,1	525	446	1572	790	315	475

Sample 1 is Vegetable Garden west borehole, number 287.

Sample 2 is Vegetable Garden east-central borehole, number 288.

Sample 3 is New Lucerne borehole, number 272.

The symbols and units used for the chemical components are the same as those used in Table J3, page J15.

TABLE J4(2)
 NATURAL SEASONAL DRIFT IN THE COMPOSITION OF WATER FROM A SINGLE BOREHOLE:
 VEGETABLE GARDEN EAST-CENTRAL, no 288

Date (1974-5)	pH	SO ₄ ⁼	CaH	MgH	TH	TDS	Cl ⁻	PA	MA
March*	6,7	166	322	375	697	971	127	nil	465
13/5**	7,16	220	365	398	760	-	220	nil	445
13/8	7,0	292	160	670	830	1224	174	nil	445
20/8	6,8	291	280	530	810	1204	173	nil	450
7/9	7,0	289	376	434	810	1252	230	nil	445
16/9	7,3	299	396	424	820	1224	179	nil	447
21/9	7,0	275	316	424	740	1168	178	nil	335
28/9	7,0	279	392	408	800	1200	173	nil	430
7/10	7,0	287	396	414	810	1160	167	nil	450
12/10	7,1	281	388	432	820	1124	165	nil	440
26/10	6,9	281	372	428	800	1236	161	nil	445
2/11	7,1	284	380	420	800	1244	158	nil	455
11/11	7,0	279	380	410	790	1252	158	nil	450
16/11	6,9	274	372	418	790	1480	156	nil	435
23/11	7,1	278	352	428	780	1180	156	nil	450
30/11	6,8	276	368	432	800	1112	154	nil	450
7/12	7,0	274	368	422	790	-	153	nil	440
14/12	6,8	273	372	418	790	1224	153	nil	455
21/12	7,0	188	352	398	750	1076	133	nil	450
29/12	6,8	279	372	428	800	1096	150	nil	445
11/1	6,8	268	372	428	800	1304	147	nil	445
18/1	6,8	254	356	424	780	1308	143	nil	430
25/1	6,8	252	352	448	790	1564	139	nil	455
8/2	7,1	253	360	430	790	1056	145	nil	415
15/2	7,0	261	368	432	800	1164	128	nil	430
22/2	6,8	261	356	434	790	1164	155	nil	415
1/3***	7,0	227	304	266	570	796	65	nil	485
8/3***	6,8	45	286	174	460	520	10	nil	480
15/3	7,1	254	340	450	790	1270	152	nil	415
25/3	7,2	252	300	460	760	1192	158	nil	406
\bar{x}	6,96	265	353	436	789	1210	160	nil	437
σ	0,15	29,95	45,89	52,68	27,22	120,60	22,87	0	24,53

The symbols and units used for the chemical components are the same as those given in Table J3, page J15.

* These are the means of several determinations made during March.

** Mean values of thirteen determinations

*** The results in this table have not been corrected for obvious gross errors. One source of gross error is the fact that the pump on this hole is connected into a general irrigation network that is linked to several widely separated boreholes. The irrigation pipes vibrate constantly and it is very difficult to tell if a particular submersible pump is running or not. If it is not, then the sample collected from the tap next to the hole may well contain water that was derived from a borehole a kilometer away and not from below.

TABLE J4(3)

SEASONAL VARIATIONS IN THE COMPOSITIONS OF BOREHOLE WATERS: BOREHOLE N^o 296

	March 1974	May 1974
Sulphate	0,4	2
CaH	440	312
MgH	220	338
TH	660	650
TDS	616	480
Cl ⁻	73	72
PA	nil	nil
MA	580	570
Cu µg/l	1,0	2
Pb µg/l	2,7	<1
Zn µg/l	32	91
Na mg/l	13,0	15
pH	7,40	7,0

BOREHOLE N^o 297

Sulphate	7	9
CaH	285	288
MgH	383	392
TH	668	680
TDS	678	544
Cl ⁻	30	34
PA	nil	nil
MA	605	690
Cu	2,4	<1
Pb	11,7	16
Zn	10200	2600
Na	16,2	18
pH	8,4*	6,7

* thought to be due to faulty meter

BOREHOLE 298

Sulphate	2	7
CaH	340	68
MgH	160	508
TH	590	576
TDS	508	648
Cl ⁻	36	36
PA	nil	nil
MA	570	590
Cu	0,9	<1
Pb	1,2	3
Zn	15	14
pH	7,10	6,8

Units of measurement for major components defined on page J15

TABLE J4(3) (cont.)

SEASONAL VARIATIONS IN THE COMPOSITIONS OF BOREHOLE WATERS: BOREHOLE N^o 300

	March 1974	May 1974
Sulphate	13	31
CaH	380	340
MgH	210	330
TH	590	670
TDS	520	556
Cl ⁻	24	74
PA	nil	nil
MA	565	540
Cu	1,1	1
Pb	2,5	4
Zn	42	22
Na	1,8	9
pH	6,90	6,7
<hr/>		
BOREHOLE 299		
Sulphate	60	37
CaH	495	464
MgH	605	566
TH	1100	1030
TDS	1491	1292
Cl ⁻	370	306
PA	nil	nil
MA	610	605
Cu	4,8	3
Pb	2,4	<1
Zn	300	184
Na	85	130
pH	6,90	6,8
<hr/>		
BOREHOLE D5		
	May 1974	March 1975
Sulphate	9	12
CaH	112	245
MgH	380	240
TH	492	485
TDS	560	508
Cl ⁻	36	9
PA	nil	nil
MA	490	492
Cu	3	-
Pb	1	-
Zn	62	-
Na	2	-
pH	6,9	7,2

TABLE J4(3) (cont.)

SEASONAL VARIATIONS IN THE COMPOSITIONS OF BOREHOLE WATERS: BOREHOLE NO 271

	March 1974	March 1975
Sulphate	42	59
CaH	270	195
MgH	264	370
TH	534	563
TDS	598	728
Cl ⁻	58	67
PA	nil	nil
MA	500	470
Cu	0,6	-
Pb	3,0	-
Zn	8,2	-
Na	11,3	-
pH	7,35	7,2
<hr/>		
BOREHOLE 287		
Sulphate	15	17
CaH	290	180
MgH	210	285
TH	500	465
TDS	466	420
Cl ⁻	18	12
PA	nil	nil
MA	486	470
Cu	9,0	-
Pb	4,8	-
Zn	42	-
Na	6,8	-
pH	6,8	7,2
<hr/>		
BOREHOLE 275		
Sulphate	6	10
CaH	240	165
MgH	235	285
TH	475	450
TDS	450	412
Cl ⁻	10	12
PA	nil	nil
MA	491	466
Cu	4,6	-
Pb	2,0	-
Zn	230	-
Na	4,1	-
pH	5,9*	7,3

* thought to be due to faulty pH meter

TABLE J4(3) (cont.)

SEASONAL VARIATIONS IN THE COMPOSITIONS OF BOREHOLE WATERS: BOREHOLE N^o 274

	March 1974	March 1975
Sulphate	11	10
CaH	225	175
MgH	226	270
TH	451	445
TDS	466	472
Cl ⁻	15	15
PA	nil	nil
MA	491	457
Cu	7,6	-
Pb	0,5	-
Zn	3,2	-
Na	5,0	-
pH	6,7	7,4
<hr/>		
BOREHOLE 283		
Sulphate	3	16
CaH	380	200
MgH	111	255
TH	491	455
Cl ⁻	24	12
PA	nil	nil
MA	486	473
Cu	4,0	-
Pb	2,5	-
Zn	10	-
Na	8,4	-
pH	7,2	7,1
<hr/>		
BOREHOLE 318		
Sulphate	193	248
CaH	210	270
MgH	469	435
TH	679	705
TDS	914	1120
Cl ⁻	146	167
PA	nil	nil
MA	473	447
Cu	22	-
Pb	4,9	-
Zn	11	-
Na	75,8	-
pH	6,6	7,2

TABLE J4(3) (cont.)

SEASONAL VARIATIONS IN THE COMPOSITIONS OF BOREHOLE WATERS: BOREHOLE N^o 273

		March 1974	March 1975
		<hr/>	
	Sulphate	13	8
	CaH	230	190
	MgH	231	270
	TH	461	460
	TDS	469	480
	Cl ⁻	15	15
	PA	nil	nil
	MA	479	465
	Cu	9,9	-
	Pb	3,0	-
	Zn	2,2	-
	Na	5,1	-
	pH	7,7	7,4
		<hr/>	
BOREHOLE 272			
	Sulphate	315	442
	CaH	145	310
(New Lucerne	MgH	395	495
Borehoie)	TH	540	805
	TDS	979	1508
	Cl ⁻	127	318
	PA	nil	nil
	MA	477	386
	Cu	24	-
	Pb	10,0	-
	Zn	3,8	-
	Na	179	-
	pH	7,6	7,0
		<hr/>	
BOREHOLE 284		March 1974	May 1974
		<hr/>	
	Sulphate	7	9
	CaH	410	88
	MgH	110	440
	TH	520	528
	TDS	511	604
	Cl ⁻	36	36
	PA	nil	nil
	MA	500	500
	Cu	0,6	<1
	Pb	0,4	2
	Zn	38	27
	Na	6,3	7
	pH	7,0	7,0
		<hr/>	

TABLE J4(3) (cont.)

SEASONAL VARIATIONS IN THE COMPOSITIONS OF BOREHOLE WATERS: BOREHOLE N^o 295

	March 1974	May 1974	March 1975
Sulphate	18	5	
CaH	440	240	
MgH	100	314	
TH	540	560	
TDS	470	584	
Cl ⁻	24	49	
PA	nil	nil	
MA	520	565	
Cu	2,0	<1	
Pb	10,2	3	
Zn	710	748	
Na	10,7	7	
pH	7,15	6,8	
<hr/>			
BOREHOLE 276			
Sulphate	208	111	70
CaH	350	108	260
MgH	202	444	255
TH	552	548	515
TDS	802	776	584
Cl ⁻	17	24	12
PA	nil	nil	nil
MA	458	455	473
Cu	2,5	4	-
Pb	0,9	<1	-
Zn	1900	712	-
Na	33,0	30	-
pH	6,7	6,8	7,1

TABLE J4(4): SUMMARY BY RANKING OF THE SEVERITY OF OBSERVED CHANGES IN THE COMPOSITIONS OF BOREHOLE WATERS AS A RESULT OF SEASONAL DRIFT

	BOREHOLE NUMBER																Summary	comment	
	284	295	296	297	298	299	300	271	D5	276	287*	275	283	274*	273*	318*			272*
Sulphate	N	N	N	N	N	N	N	N	N	M	N	N	N	N	N	N	M	15N2M	very good
CaH	S	S	S	N	S	M	N	M	S	S	S	S	S	M	M	M	S	2N5M10S	poor
MgH	S	S	S	N	S	M	M	S	S	M	M	M	S	M	M	N	S	2N7M8S	poor
TH	N	N	N	N	N	M	M	N	N	N	M	N	M	N	N	N	S	12N4M1S	good
TDS	M	M	M	M	M	M	N	M	N	M	N	N	M	N	N	M	S	6N10M1S	moderate
Cl	N	N	N	N	N	N	M	N	M	N	N	N	N	N	N	N	M	14N3M	very good
PA	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	17N	no variation
MA	N	N	N	M	N	N	N	N	N	N	N	N	N	M	N	N	M	14N3M	very good
Cu	N	N	N	N	N	N	N	-	-	N	-	-	-	-	-	-	-	8N	excellent
Pb	N	M	N	N	N	N	N	-	-	N	-	-	-	-	-	-	-	7N1M	very good
Zn	N	N	M	M	N	M	N	-	-	M	-	-	-	-	-	-	-	4N4M	good
Na	N	N	N	N	N	M	N	-	-	N	-	-	-	-	-	-	-	7N1M	very good
pH	N	M	M	S	M	N	N	N	M	M	M	S	N	S	M	S	S	5N7M5S	poor
S-values	2	2	2	1	2	0	0	1	2	1	1	2	2	1	0	1	5		

Boreholes marked * are heavily pumped. The symbols and units used for the chemical components are given on pages J15 and J21. N = negligible change between sampling events. M = moderate change. S = severe change. Based on data from Table J4(3).

APPENDIX K

Listing of the computer program that produced the hydrogeochemical data maps (variants of Map 4)

The program listed in the following pages was designed specifically to plot hydrogeochemical data on a simplified cadastral map of the Otavi Mountainland. These maps are in Volume II and are numbered 4c, 4d etc. The symbolic listing reproduced here illustrates some of the routines that could be used in similar graphical programs that might be suitable for use in other exploration projects. The main features of this program are that it (i) draws geographical features from data taken off conventional maps on a digitizer table. (ii) plots sampling points, with the sample value next to the point, from an X-Y-Z array. (iii) is "intelligent", in that it positions the sample values so that they are neatly placed alongside the sampling point, but never overwrite the symbols for the sampling points, or other analytical values occurring nearby. (iv) adjusts the scale of the whole plot to any selected size.

The program is in FORTRAN IV and used standard Calcomp graphics calls /1208/. Some calls are to the UCT GDP package /1196/ and will not operate on other systems. Nevertheless these special calls could very easily be replaced by equivalent statements in standard Calcomp format.

```

C THIS PROGRAM RESIDES IN JWMWITH. IN SYMBOLIC AND ABSOLUTE FORMS.
C ITS NAME IS JWMWITHPLOT.
C X AND Y ARE DIGITIZER CO-ORDINATES.
C EMVAL ARE THE M-SERIES CHEMICAL VALUES (2ND ORIENTATION STUDY).
C EDVAL ARE THE D-SERIES CHEMICAL VALUES (APPLICATION STUDY).
C
C *****
C
C   DIMENSION X(500),Y(500),EMVAL(60),EDVAL(200),ELNAME(12),FMTM(4),
C   CFMTD(4),IZM(500),IZD(500)
C   DATA INP, IOP /8,5/
C   REAL LU1M,LU2M,LL1M,LL2M,LU1D,LU2D,LL1D,LL2D
C 10 FORMAT(1X,FS.1,1X,FS.1)
C 20 FORMAT(12A6)
C 30 FORMAT(4A6)
C 40 FORMAT(2I2,F6.0)
C 42 FORMAT(10F6.0)
C SET ALL IZ VALUES TO ZERO
C DO 48 N=1,500
C   IZM(N)=0
C   IZD(N)=0
C 48 CONTINUE
C THE DUMMY ARGUMENTS FTMX SELECT ELEMENTS FROM THE DATA READ FROM
C (JWMWITH.SOMEDATAELEMENTOROTHER) E.G: .TDS AND .XP9
C   READ(INP,30)FMTM
C   READ(INP,30)CFMTD
C   READ(INP,20)ELNAME
C   READ(INP,40)IFLAG,NDEC,VMULT
C   READ(INP,42)DSF,SCALE,LL1M,LL2M,LU1M,LU2M,LL1D,LL2D,LU1D,LU2D
C THE THRESHOLD VALUES MUST BE ADJUSTED FOR THE
C MULTIPLICATION FACTOR VMULT.
C   LU1M=LU1M*VMULT
C   LU2M=LU2M*VMULT
C   LL1M=LL1M*VMULT
C   LL2M=LL2M*VMULT
C   LU1D=LU1D*VMULT
C   LU2D=LU2D*VMULT
C   LL1D=LL1D*VMULT
C   LL2D=LL2D*VMULT
C
C *****
C
C ELNAME IS THE ELEMENT SELECTED FROM THE BLOCK OF CHEMICAL ANALYSES ATADDED
C
C IFLAG IS 1 WHEN ONLY M DATA ARE USED, 2 WHEN BOTH M AND D DATA ARE USED,
C 3 WHEN D75 IS ALSO PRESENT AND 4 FOR PH, WHERE THE PRECISION OF
C DETERMINATION IS NOT THE SAME FOR D AND M. IF IFLAG IS 3 THEN DSF
C MUST BE PICKED UP FROM A FIFTH CARD.
C
C DSF IS THE VALUE FOR SAMPLE D75, WHICH IS NOT PRESENT IN SOME MAPS.
C FOR CONVENIENCE, THE SCALE FACTOR FOR THE WHOLE PLOT IS ALSO READ
C FROM CARD 5, WHILE THE NUMBER OF DECIMALS TO BE USED WHEN THE
C DATA ARE PLOTTED IS ENTERED AS NDEC ON CARD 4.
C
C NDEC= -1 GIVES NO DECIMALS; NDEC = (+)N GIVES N DECIMALS.
C
C VMULT IS A MULTIPLICATION FACTOR THAT WILL BE USED FOR
C XRF DATA, RATIOS, ETC.
C *****NB***** THE DEFAULT VALUE IS 1.0 AND MUST BE GIVEN.
C
C THUS THE FIRST FIVE LINES OF THE WELDED DATA ELEMENT MUST BE UPDATED FOR EACH

```

```

C PLOT. THESE FIVE ARE FOLLOWED BY THE DIGITIZER DATA, THE M DATA AND FINALLY
C THE D DATA. THE NAME OF THE WELDED ELEMENT IS .JWMWITHALL(N),
C WHERE N =1,2,3 ETC. AND REPRESENTS UPDATED OR EXPANDED
C VERSIONS OF THE BASIC DATA PACK.
C VERSION (N+1) WILL ALWAYS INCLUDE ALL DATA FOR VERSION N
C AND ONLY SMALL CHANGES IN FMTM AND FMTD WILL BE REQUIRED
C IN ORDER TO XQT EARLIER PLOTS WITH THE UPDATED DATAPACK.
C
C ANNEXURE: PLOTTING IN COLOUR.
C IZM(N) AND IZD(N) ARE FLAGS THAT ALLOW THE SYMBOLS OF
C FOUR GRADES OF *****ANOMALOUS SAMPLES *****
C TO BE PLOTTED IN RED (+ANOMALIES) OR GREEN (-ANOMALIES).
C LU1M,LU2M,LL1M,LL2M,LU1D,LU2D,LL1D AND LL2D ARE THE
C LOWER AND UPPER, GRADE I AND GRADE II THRESHOLD VALUES FOR
C THE M-SERIES AND D-SERIES SAMPLES.
C
C *****
C
C DO 50 N=1,489
C READ(INP,10) X(N),Y(N)
50 CONTINUE
C DO 60 N=1,54
C READ(INP,FMTM)EMVAL(N)
60 CONTINUE
C THE D DATA ARE NOT PRESENT AND THEREFORE CANNOT BE READ IF IFLAG = 1.
C IF (IFLAG.EQ.1)GO TO 75
C DO 70 N=1,162
C READ(INP,FMTD)EDVAL(N)
70 CONTINUE
75 DO 80 N=1,489
C X(N)=X(N)/SCALE
C Y(N)=Y(N)/SCALE
80 CONTINUE
C THIS ADJUSTS THE SCALE OF THE WHOLE PLOT.
C INITIALIZE THE PLOT AND CALL FOR INK PENS.
C CALL PLOTS(0,0,0)
C THE NEW PLOTTER IS METRICATED. THEREFORE A NEW SCALING
C FACTOR MUST BE INTRODUCED.
C CALL FACTOR(2.54)
C CALL OPMS(37,'PLS LOAD P1-BK/I3, P2-GN/I3, P3-RD/I3')
C CALL PAGESIZ(57.94,40.56)
C CALL BLACK PEN
C CALL NEWPEN(1)
C PLOT SYMBOLS REPRESENTING THE TOWNS.
C CALL DSYMBL(X(1),Y(1),0.14,1,0.)
C CALL DSYMBL(X(2),Y(2),0.28,1,0.)
C CALL DSYMBL(X(3),Y(3),0.14,1,0.)
C PLOT THE NAMES OF THE THREE TOWNS.
C CALL SYMBOL(X(4),Y(4),0.14,5HOTAVI,0.,5)
C CALL SYMBOL(X(5),Y(5),0.14,6HTSUMEB,0.,5)
C CALL SYMBOL(X(6),Y(6),0.14,12HGROOTFONTEIN,0.,12)
C PLOT THE TITLE OF THE DRAWING
C CALL SYMBOL(X(7),Y(7),0.21,ELNAME,0.,72)
C PLOT THE BOUNDARIES OF THE WITHDRAWAL AREA.
C CALL MOVE(X(8),Y(8))
C DO 400 N=9,52
C CALL DRAW(X(N),Y(N))
400 CONTINUE
C CALL DRAW(X(8),Y(8))
C PLOT THE DATA FOR THE M-SERIES SAMPLES NEXT TO WHERE
C THE APPROPRIATE SAMPLING POINT WILL FALL.
NN=0

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DO 600 N=107,160
NN=NN+1
C IF XRF DATA, ETC. ARE TO BE USED MULTIPLICATION MAY BE EFFECTED.
  EMVAL(NN)=EMVAL(NN)*VMULT
C THE NEXT OF IF STATEMENTS SERVES TWO PURPOSES:
C (1) CONTROL OF PRECISION WITHIN THE PLOT ITSELF. E.G.,
C THE VALUES 6.4 AND 64 (AS OPPOSED TO 64.0) CAN BOTH APPEAR:1.E.,
C NDEC IS VARIED AS EMVAL VARIES.
C (2) THOSE NUMBERS THAT PLOT TO THE LEFT OF THEIR ASSOCIATED
C SYMBOLS ARE RIGHT JUSTIFIED WHATEVER THE NUMBER OF CHARACTERS
C PLOTTED. E.G., IF X IS A PLOTTED POINT, THE PLOTTED VALUE
C NEXT TO IT ON THE LEFT WILL APPEAR AS FOLLOWS:
C (A)(SAY, HCO3): 534 X (B)(SAY,CL): 53 X (C)(SAY,PB): 5 X (NOT'S X)
  NDEC=NDEC
  IF(NDUC.EQ.2) GO TO 550
  IF(NDUC.EQ.1) GO TO 560
  IF(NDUC.EQ.-1) GO TO 570
550 ISCORE=4
  IF(EMVAL(NN).GT.9.99999) NDEC=1
  IF(EMVAL(NN).GT.99.99999) NDEC=-1
  GO TO 568
560 IF(EMVAL(NN).LT.10.) ISCORE=3
  IF(EMVAL(NN).GT.9.99999) NDEC=-1
565 IF(EMVAL(NN).GT.9.99999) ISCORE=2
568 IF(EMVAL(NN).GT.99.99999) ISCORE=3
  IF(EMVAL(NN).GT.999.99999) ISCORE=4
  IF(EMVAL(NN).GT.9999.99999) ISCORE=5
  IF(EMVAL(NN).GT.99999.99999) GO TO 960
C OVERFLOW SITUATION: A WARNING WILL BE PLOTTED.
  GO TO 590
570 ISCORE=1
  GO TO 565
590 CONTINUE
  IF(N.EQ.110) GO TO 595
  IF(N.EQ.121) GO TO 595
  IF(N.EQ.127) GO TO 595
  IF(N.EQ.128) GO TO 595
  IF(N.EQ.144) GO TO 595
  IF(N.EQ.153) GO TO 595
  IF(N.EQ.158) GO TO 595
  IF(N.EQ.159) GO TO 595
  GO TO 598
595 IF(ISCORE.EQ.2) X(N)=X(N)-(1.78/SCALE)
  IF(ISCORE.EQ.3) X(N)=X(N)-(3.56/SCALE)
  IF(ISCORE.EQ.4) X(N)=X(N)-(5.34/SCALE)
  IF(ISCORE.EQ.5) X(N)=X(N)-(7.12/SCALE)
598 CALL NUMBER(X(N),Y(N),0.07,EMVAL(NN),0.,NDEC)
C SET THE FLAG THAT WILL ALLOW COLOURING OF THE SYMBOL ASSOCIATED
C WITH ANOMALOUS SAMPLES.
  IF(EMVAL(NN).LT.LL2M) IZM(NN)=2
  IF(EMVAL(NN).LT.LL1M) IZM(NN)=1
  IF(EMVAL(NN).GT.LU2M) IZM(NN)=3
  IF(EMVAL(NN).GT.LU1M) IZM(NN)=4
600 CONTINUE
C PLOT THE SYMBOLS FOR THE M-SERIES SAMPLING POINTS.
C NEGATIVE ANOMALIES IN GREEN (TWO TYPES OF SYMBOL)
C POSITIVE ANOMALIES IN RED (TWO TYPES OF SYMBOL)
C BACKGROUND VALUES IN BLACK (ONE TYPE OF SYMBOL)
  NN=0
  DO 650 N=53,106
  NN=NN+1
  IF(IZM(NN).EQ.0) CALL NEWPEN(1)

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IF (IZM(NN).EQ.1) CALL NEWPEN(2)
IF (IZM(NN).EQ.2) CALL NEWPEN(2)
IF (IZM(NN).EQ.3) CALL NEWPEN(3)
IF (IZM(NN).EQ.4) CALL NEWPEN(3)
IF (IZM(NN).EQ.0) CALL DSYMBL(X(N),Y(N),0.07,0,0.)
IF (IZM(NN).EQ.1) CALL DSYMBL(X(N),Y(N),0.07,0,0.)
IF (IZM(NN).EQ.1) CALL DSYMBL(X(N),Y(N),0.07,11,0.)
IF (IZM(NN).EQ.2) CALL DSYMBL(X(N),Y(N),0.07,0,0.)
IF (IZM(NN).EQ.3) CALL DSYMBL(X(N),Y(N),0.07,0,0.)
IF (IZM(NN).EQ.4) CALL DSYMBL(X(N),Y(N),0.07,0,0.)
IF (IZM(NN).EQ.4) CALL DSYMBL(X(N),Y(N),0.07,11,0.)
650 CONTINUE
C THE STEPS FOR PLOTTING THE D DATA MUST BE BYPASSED IF IFLAG IS 1.
IF (IFLAG.EQ.1) GO TO 810
C PLOT THE DATA FOR THE D-SERIES SAMPLES NEXT TO WHERE THE
C APPROPRIATE SAMPLING POINT WILL FALL.
CALL NEWPEN(I)
NN=0
DO 800 N=323,484
NN=NN+1
C MULTIPLICATION MAY BE APPLIED TO RATIOS, ETC.
EDVAL(NN)=EDVAL(NN)*VMULT
704 NDCU=NDEC
IF (IFLAG.EQ.4) GO TO 780
IF (NDCU.EQ.2) GO TO 750
IF (NDCU.EQ.1) GO TO 760
IF (NDCU.EQ.-1) GO TO 770
750 ISCORE=4
IF (EDVAL(NN).GT.9.99999) NDCU=1
IF (EDVAL(NN).GT.99.99999) NDCU=-1
GO TO 768
760 IF (EDVAL(NN).LT.10) ISCORE=3
IF (EDVAL(NN).GT.9.99999) NDCU=-1
765 IF (EDVAL(NN).GT.9.99999) ISCORE=2
768 IF (EDVAL(NN).GT.99.99999) ISCORE=3
IF (EDVAL(NN).GT.999.99999) ISCORE=4
IF (EDVAL(NN).GT.9999.99999) ISCORE=5
IF (EDVAL(NN).GT.99999.99999) GO TO 960
C OVERFLOW SITUATION: A WARNING WILL BE PLOTTED.
GO TO 790
770 ISCORE=1
GO TO 765
780 FIDDLE=EDVAL(NN)*10.
IDDLE=IFIX(FIDDLE)
FOODLE=FIDDLE-IDDLE
IF (FOODLE.LT.0.05) NDCU=1
IF (FOODLE.LT.0.05) ISCORE=3
IF (FOODLE.GT.0.05) NDCU=2
IF (FOODLE.GT.0.05) ISCORE=4
790 IF (N.EQ.341) GO TO 795
IF (N.EQ.345) GO TO 795
IF (N.EQ.369) GO TO 795
GO TO 798
795 IF (ISCORE.EQ.2) X(N)=X(N)-(1.78/SCALE)
IF (ISCORE.EQ.3) X(N)=X(N)-(3.56/SCALE)
IF (ISCORE.EQ.4) X(N)=X(N)-(5.34/SCALE)
IF (ISCORE.EQ.5) X(N)=X(N)-(7.12/SCALE)
798 CALL NUMBER(X(N),Y(N),0.07,EDVAL(NN),0.,NDCU)
C SET THE FLAG THAT WILL ALLOW EMPHASIS OF THE SYMBOLS
C ASSOCIATED WITH ANOMALOUS SAMPLES.
IF (EDVAL(NN).LT.LL2D) IZD(NN)=2
IF (EDVAL(NN).LT.LL1D) IZD(NN)=1

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      IF (EDVAL(NN).GT.LU2D) IZD(NN)=3
      IF (EDVAL(NN).GT.LUID) IZD(NN)=4
800 CONTINUE
C PLOT THE SYMBOLS FOR THE D-SERIES SAMPLES IN COLOURS (CF. M-SERIES).
  NN=0
  DO 805 N=161,322
  NN=NN+1
  IF (IZD(NN).EQ.0) CALL NEWPEN(1)
  IF (IZD(NN).EQ.1) CALL NEWPEN(2)
  IF (IZD(NN).EQ.2) CALL NEWPEN(2)
  IF (IZD(NN).EQ.3) CALL NEWPEN(3)
  IF (IZD(NN).EQ.4) CALL NEWPEN(3)
  IF (IZD(NN).EQ.0) CALL DSYMBL(X(N),Y(N),0.07,5,0.)
  IF (IZD(NN).EQ.1) CALL DSYMBL(X(N),Y(N),0.07,11,0.)
  IF (IZD(NN).EQ.2) CALL DSYMBL(X(N),Y(N),0.07,5,0.)
  IF (IZD(NN).EQ.3) CALL DSYMBL(X(N),Y(N),0.07,5,0.)
  IF (IZD(NN).EQ.4) CALL DSYMBL(X(N),Y(N),0.07,11,0.)
805 CONTINUE
C PLOT THE BAR SCALE
810 CALL NEWPEN(1)
  DO 900 N=485,489
  CALL DSYMBL(X(N),Y(N),0.14,13,0.)
900 CONTINUE
  XSTART=317.9/SCALE
  YSTART=29.2/SCALE
  XEND=397.8/SCALE
  CALL MOVE(XSTART,YSTART)
  CALL DRAW(XEND,YSTART)
C PLOT THE LEGEND FOR THE BAR SCALE
  XZERO=316.4/SCALE
  XONE=336.4/SCALE
  XTWO=354.9/SCALE
  XTHREE=374.9/SCALE
  XFOUR=394.9/SCALE
  YCOMM=22.2/SCALE
  CALL SYMBOL(XZERO,YCOMM,0.14,1H0,0.,1)
  CALL SYMBOL(XONE,YCOMM,0.14,1H5,0.,1)
  CALL SYMBOL(XTWO,YCOMM,0.14,2H10,0.,2)
  CALL SYMBOL(XTHREE,YCOMM,0.14,2H15,0.,2)
  CALL SYMBOL(XFOUR,YCOMM,0.14,6H20 KM.,0.,6)
C IF IFLAG IS 3 THE D(75) VALUE MUST BE PLOTTED.
  IF (IFLAG.EQ.1) GO TO 950
  IF (IFLAG.EQ.2) GO TO 940
  XSFS=344.1/SCALE
  YSFS=233.3/SCALE
  XSFT=341.8/SCALE
  YSFT=235.6/SCALE
  DSF=DSF*VMULT
  IF (DSF.LT.LL2D) IZD(500)=2
  IF (DSF.LT.LL1D) IZD(500)=1
  IF (DSF.GT.LU2D) IZD(500)=3
  IF (DSF.GT.LUID) IZD(500)=4
  CALL NUMBER(XSFT,YSFT,0.07,DSF,0.,NDEC)
  IF (IZD(500).EQ.0) CALL NEWPEN(1)
  IF (IZD(500).EQ.1) CALL NEWPEN(2)
  IF (IZD(500).EQ.2) CALL NEWPEN(2)
  IF (IZD(500).EQ.3) CALL NEWPEN(3)
  IF (IZD(500).EQ.4) CALL NEWPEN(3)
  IF (IZD(500).EQ.0) CALL DSYMBL(XSFS,YSFS,0.07,5,0.)
  IF (IZD(500).EQ.1) CALL DSYMBL(XSFS,YSFS,0.07,11,0.)
  IF (IZD(500).EQ.2) CALL DSYMBL(XSFS,YSFS,0.07,5,0.)
  IF (IZD(500).EQ.3) CALL DSYMBL(XSFS,YSFS,0.07,5,0.)

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      IF (IZD(500).EQ.4) CALL DSYMBL(XSFS,YSFS,0.07,11,0.)
      CALL NEWPEN(1)
C
C *****
C PLOTTING LEGENDS: WITH A NOTE ON HOW TO WRITE
C RACIST POETRY IN FORTRAN.
C *****
C
940  XXM=410./SCALE
      YXM=150./SCALE
      CALL SYMBOL (XXM,YXM,0.14,26HOIAMDONS: APPLICATION DATA,0.,26)
      XHE=410./SCALE
      XHOLAS=410./SCALE
      XLET=410./SCALE
      XHIM=410./SCALE
      XGO=410./SCALE
      YHE=110./SCALE
      YHOLAS=100./SCALE
      YLET=90./SCALE
      YHIM=80./SCALE
      YGO=70./SCALE
      CALL DSYMBL (XHE,YHE,0.14,5,0.)
      CALL NEWPEN(2)
      CALL DSYMBL (XHOLAS,YHOLAS,0.14,5,0.)
      CALL DSYMBL (XLET,YLET,0.14,11,0.)
      CALL NEWPEN(3)
      CALL DSYMBL (XHIM,YHIM,0.14,5,0.)
      CALL DSYMBL (XGO,YGO,0.14,11,0.)
      CALL NEWPEN(1)
C THIS PLOTTED, WHERE APPROPRIATE, THE OPTIONAL PART OF THE LEGEND.
950  CONTINUE
      XXD=410./SCALE
      YXD=130./SCALE
      CALL SYMBOL (XXD,YXD,0.14,25HSQUARES: ORIENTATION DATA,0.,25)
      XEENY=420./SCALE
      XMEENY=420./SCALE
      XMYNY=420./SCALE
      XMO=420./SCALE
      XCACHA=420./SCALE
      XNIGGA=430./SCALE
      XBY=430./SCALE
      XHIS=430./SCALE
      XTOE=430./SCALE
      XIF=430./SCALE
      YEENY=110./SCALE
      YMEENY=100./SCALE
      YMYNY=90./SCALE
      YMO=80./SCALE
      YCACHA=70./SCALE
      YNIGGA=108.25/SCALE
      YBY=98.25/SCALE
      YHIS=88.25/SCALE
      YTOE=78.25/SCALE
      YIF=68.25/SCALE
      CALL DSYMBL (XEENY,YEENY,0.14,0,0.)
      CALL NEWPEN(2)
      CALL DSYMBL (XMEENY,YMEENY,0.14,0,0.)
      CALL DSYMBL (XMYNY,YMYNY,0.14,0,0.)
      CALL DSYMBL (XMO,YMO,0.14,11,0.)
      CALL NEWPEN(3)
      CALL DSYMBL (XMO,YMO,0.14,0,0.)
      CALL DSYMBL (XCACHA,YCACHA,0.14,0,0.)

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```
CALL DSYMBL(XCACHA,YCACHA,0.14,11,0.)
CALL NEWPEN(1)
CALL SYMBOL(XNIGGA,YNIGGA,0.14,16HBACKGROUND VALUE,0.,16)
CALL SYMBOL(XBY,YBY,0.14,21HWEAK NEGATIVE ANOMALY,0.,21)
CALL SYMBOL(XHIS,YHIS,0.14,23HSTRONG NEGATIVE ANOMALY,0.,23)
CALL SYMBOL(XTOE,YTOE,0.14,21HWEAK POSITIVE ANOMALY,0.,21)
CALL SYMBOL(XIF,YIF,0.14,23HSTRONG POSITIVE ANOMALY,0.,23)
C THIS PLOTTED THE OTHER PART OF THE LEGEND
GO TO 990
C WARNING CONTINGENCY OWING TO OVERFLOW.
960 XXD=410.0/SCALE
YXD=150./SCALE
CALL SYMBOL(XXD,YXD,0.4,7HWARNING,0.,7)
C THE POPE IS A JEW.
990 CALL ENDPLT
STOP
END
```

APPENDIX L

Instructions given to field personnel collecting water samples during the application phase of the hydrogeochemical exploration project, with footnotes showing the minor changes that were made in practice during sampling

"the pump don't work

'cause the vandals took the handles...." /203/

SAMPLING PROCEDURES

A. PREPARATION OF BOTTLES

1. Use high density polyethylene bottles (Consol Glass 0222).
2. Leach bottle with perchloric acid¹ for 48 hours before use.
3. Label bottles on lids²- use wax pencil.
4. Bottles to be marked at 800 ml level.

B. PREPARATIONS AT SITE OF SAMPLING

1. Visit the site of the borehole and obtain farmer's permission to sample.
2. Note whether the pump and piping is suitable for providing a sample.
3. Note any special requirements e.g. monkey-wrench, V-belts, keys for gates.
4. Ask of farmer when borehole was drilled. Depth at which water was struck. Rate of flow. Geological information.
5. Tag borehole with metal tag bearing identification number.

C. SAMPLING

1. Transport bottles in milk crates³ kept in a large plastic bag. Renew the bag regularly.
2. Transport concentrated nitric acid in the bottle⁴ in a plastic bag.
3. Run the pump for a minimum of 10 minutes. Increase the time to 20 min. if the borehole is new or if it has not been pumped regularly.
4. While the pump is running, clean the mouth of the outlet pipe of algae, etc.
5. Do not touch the mouth of the pipe with the sampling bottle.
6. Take the temperature of the water issuing from the pipe.⁵
7. Take six samples per borehole.

8. Rinse the bottle five times before taking the sample. Rinsing procedure: fill the bottle to the brim and pour out the contents, rinsing the lid in the process.
9. Four of the six samples are for cation analysis.⁶ Fill these to the 800ml mark and add 20 ml of nitric acid¹. Replace the lid and mix the contents by shaking. Remove the lid to release CO₂, then replace it. These samples must be clearly marked "for freezing" and kept in a separate crate.
- 10? To one of the four samples mentioned in (9) the following procedure must be adopted: rinse the bottle as in (8), add 800 ml of sample, take the pH of the water, add 20 ml of nitric acid, mix thoroughly, and take the pH again. This is for the determination of alkalinity.
11. For the other two samples: fill to the brim after rinsing as in (8). Replace lid and replace in the crate set aside for samples that are to be used for anionic analyses.⁸
12. Drive slowly over farm tracks to avoid unnecessary agitation of the samples and contamination by dust.

FOOTNOTES

1. Nitric acid may be used for leaching. Perchloric acid was used in the field in place of nitric acid. See Chapter 6, part 6.2, for details.
2. It proved to be impractical to label the lids. The top portions of the bottles were marked instead.
3. Cool-chests were also used and were found to be satisfactory.
4. An autodispenser made only of glass and Teflon was used.
5. Temperature was in fact not measured, because the orientation study had shown that it was not important to do so, The pH of the sample was measured in the laboratory, as tests had shown that the pH was stable for at least 48 hours (Appendix J).
6. i.e., trace element analysis.
7. This procedure for alkalinity was based on Loewenthal's work /23/. It was found to be unnecessary, because the alkalinity readings are stable for several days (Appendix J). The whole of step (10) was therefore omitted.
8. i.e. routine wet chemical determinations of the major components.