The Analysis of Trace Lead, Cadmium, and Zinc Levels in Antarctic Soils

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Authors Note:-

There results presented here are the initial efforts of five weeks work. The hours spent on the project well exceed five hundred hours, from the initial preparation, to the development of standards and time spent operation the Atomic Absorbance equipment.

The results, are from an initial study and will be confirmed and varified in future tests. The high lead concentrations samples will imparticular be the focus of future tests.

Thus the research is by no means complete.

This project is a large assignment, which in hind-sight I did not realise when I began. I am an organic chemist. This project is a full honours project for an analytical chemist. Therefore I have had to quickly learn a great deal more skills in a branch of chemistry which I knew little about.

For the last month and a half I have essentually had two honours project in motion both requiring a lot of time and energy. Switching from organic peptide synthesis to analytic soil heavy metal testing has not been an easy task.

The results and presentation of them is thus not complete and I believed their was no reason to present them as such. I intend to complete the testing and present a bound copy of the results and expt to you and Antarctic New Zealand by the end of the year. Please accept a full copy of my log book however to satisfy the course requirement.

Please note, at the present all results are strickly confidential and are property of H.K. Powell and Mark Patton, Chemistry Department, University of Canterbury. Untill analysis is complete no part of the data should be quoted or referenced to.

The results do however show interesting trends particular in the areas of human activity and thus there results can be seen to give a models for final results.

Thanks

Attention   MARK PATON

Organisation   CHEMISTRY DEPARTMENT, UoC

Fax No.   364 2180

From   REBECCA GEE

Date   29/1/99   Time   1:25 PM   Page 1 of 1

ROUTINE
URGENT

Mark,

I have contacted Emma Waterhouse and ~~there~~ confirmed there are no problems at all with your project plans. With regard to soil disposal after your work, there is a contaminate rock dump at Scott Base. The science technician will be able to advise you down there.

All the best,

Rebecca.

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antarctic - studies @ cant. canterbury. ac. nz

Cassandra Graber
Antarctic Support Associates
61 Inverness St. 300
Englewood CO

graberca @asa.gov

Soil Chemists: KIZB

k. powell @ chem.
canterbury. ac. nz

Still have to write too:
PHIL PARFET, ASA, DENVER
FUELS Compositions of JP8/5P5

800 - 688 - 8606 X 3450

Solutions for Mark Paton (Antarctic Studies)

1   Bottle   2M Nitric Acid (HNO3)
     "Safebreak"   2 mol/litre (dilute)
     glass   500 mls

2   Plastic bottle Distilled water
                     2 x 500mls

Storage: All bottles carried in polystyrene box in bubble packing. Polystyrene box in cardboard box .

Expt: Analysis of Pb, Zn, Cd in Antarctic soil samples

Aim: To analyse the heavy metals found in Antarctic soil samples collected from Scott Base and McMurdo sounds. The 2 km road connecting the two bases was tested at 3 selected places, above, in and below the road.

Method: 1) A 5g soil sample is collected from the selected sites. (see Map) The ground soil is seived and stored in a small bag.

2) In the wet lab, the sample was weighed into storage bottle and 25ml of 2M HNO_3 added.

3) The samples were mixed and left for 37 hours.

4) After this time the filtrate was filtered in to a clean storage bottle and returned for analysis in Christchurch.
Not: Maximum of 10ml collected.

5) Analysis involved Electrothermal Atomic Absorption Spectroscopy.

Set up Procedure: 1) All sample collection jars, syringes, filter systems, spades, etc were washed in detergent and hot water. Following this they were rinsed twice in distilled water.

2) The equipment was then left in 10% HNO_3 for 24hrs. After this they were washed in double distilled water.

3) the equipment was then transferred to the clean

room where they were left to soak for 24 hrs in 10% Aristar HNO_3. Following this the equipment was left to soak in Milli Q (distilled) water.

4/ finally everything was left to dry and after this, was packed into two layers of plastic bags.

- Solution taken to Scott Base:-
  - Milli Q Distilled water (x2)
  - 2M HNO_3 (made from aristar HNO_3)

Equipment :-
  - 30, 50ml sample bottles.
  - 2 syringes
  - 1 filter (with (to) suction rings)
  - filter paper ~ 0.45μm
  - spade.
  - sieve / brush.
  - plastic disposable gloves
  - bags.
  - polythene sheeting / parafilm

field: Changes made include samples taken from the far side of the road on the upwards and downward slopes, plus the center
  ↳ unable to scale high up slopes above road.

Note · US may be spreading soil on the road at the end of each season thus lead maybe ~~found~~ found at stratified layers.
  - fuel used: JP5 and JP8 designed for Antarctic programme to reduce temperature of freezing (~-60°C)
  - Control taken from Black Island. Plains SP fly over top of area when flying into Pegusus Runway but low level of human activity. In allocated time best place to take "control" sample from. Any pollution there maybe due to wind currents of pollutant fuel from plains or natural abundance. (most likely)

  planes

Map from Emma Waterhouse 'Environmental Impact' resource

Legend For Potential Sites:

- ⬛ 0-2 Degree Slope
- ▦ 2-4 Degree Slope
- ▥ 4-6 Degree Slope
- ▤ 6-8 Degree Slope
- ☐ 8-10 Degree Slope

General Legend:

- Roads
- Tracks and Storage Areas
- Existing Buildings
- Features of Interest
- Services
- Williams Field Fuel Line (approximate location)

Alternative JP-8 Tank Relocation Site (Former U.S. Fuel Storage Site)

Proposed JP-8 Tank Relocation Site

Helo Pads

Existing JP-8 Tanks

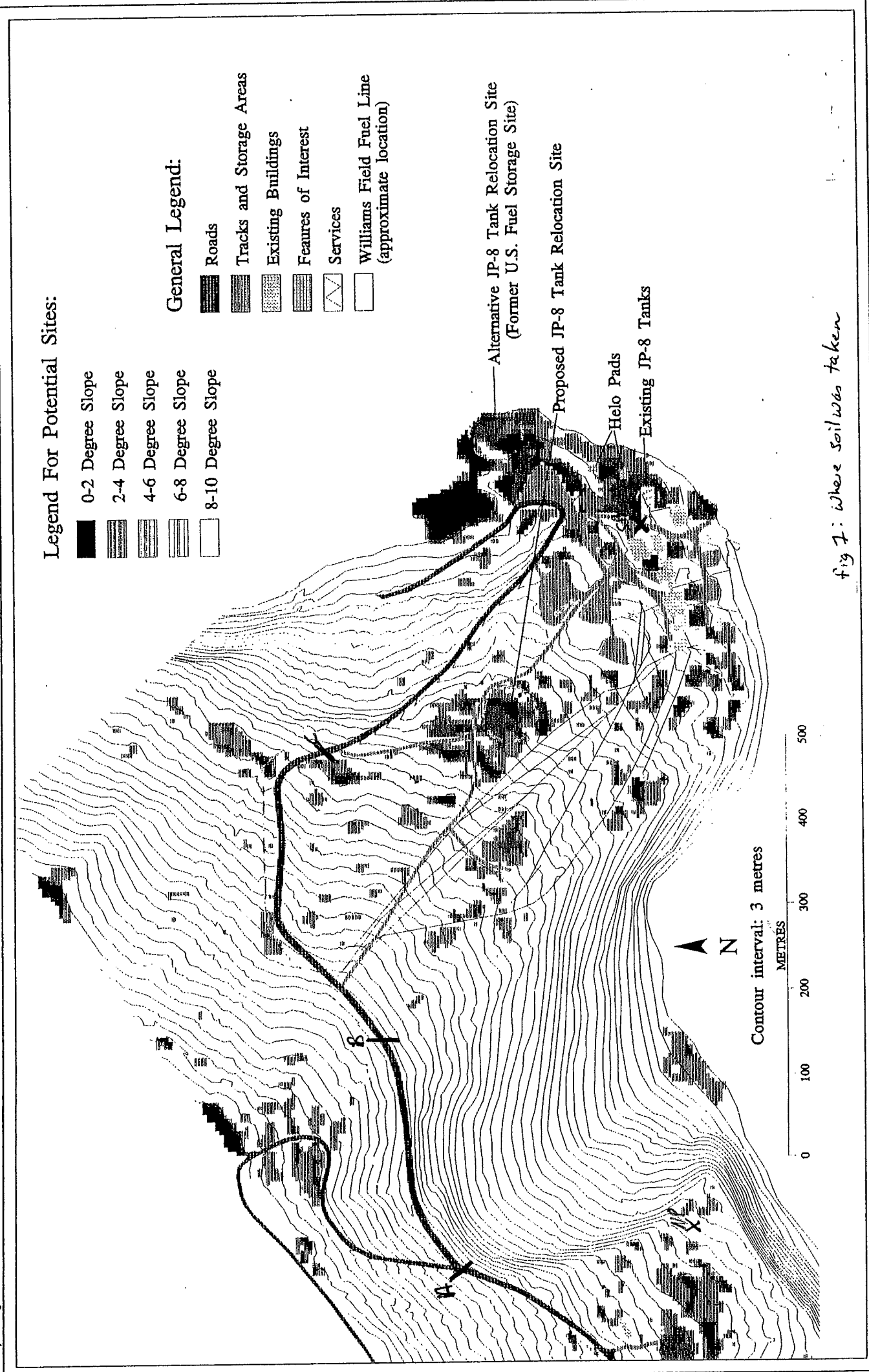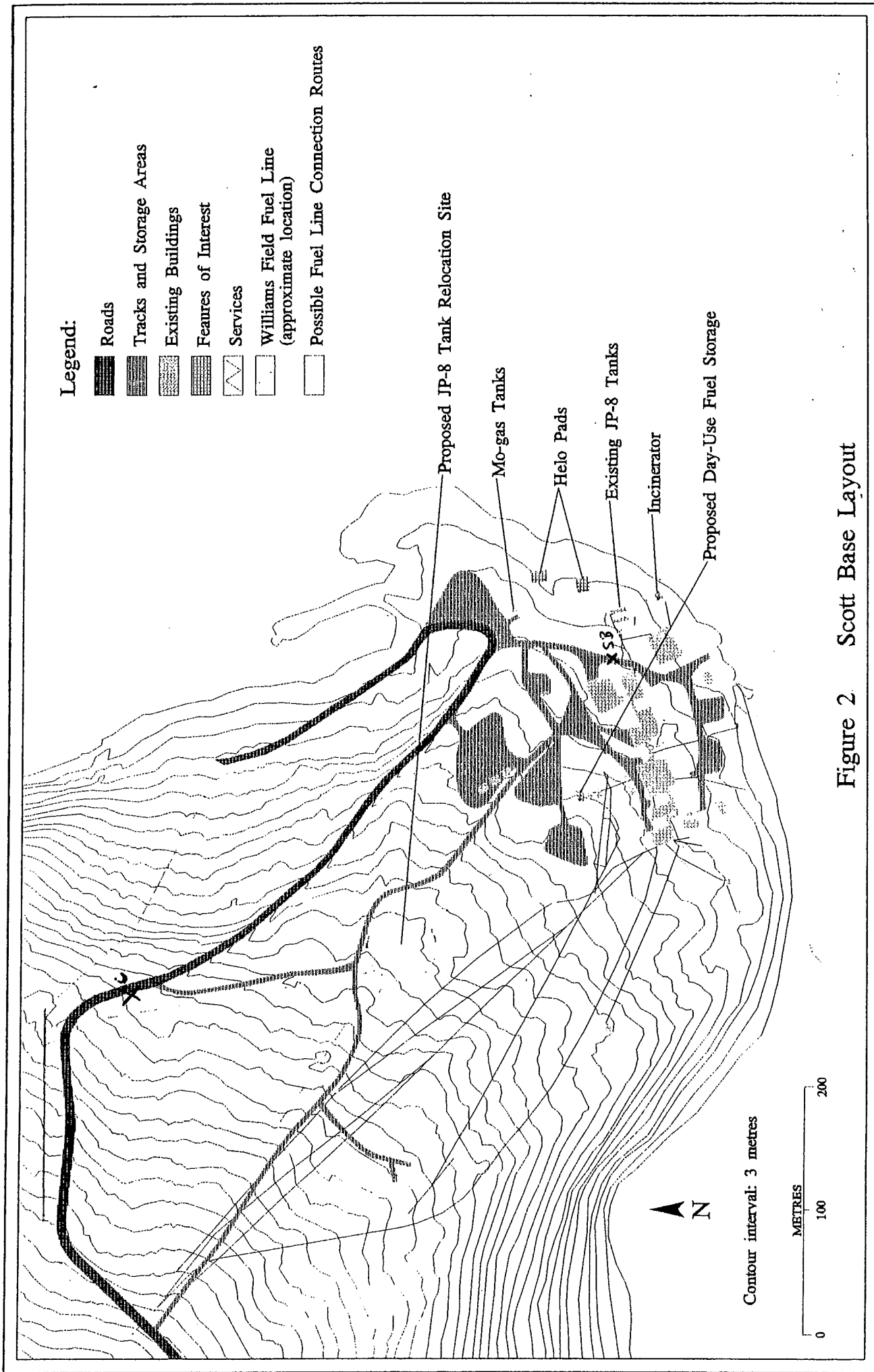Contour interval: 3 metres

METRES

0   100   200   300   400   500

N

Fig 7: Where soil was taken

Figure 2   Scott Base Layout

Legend:

Roads

Tracks and Storage Areas

Existing Buildings

Feaures of Interest

Services

Williams Field Fuel Line
(approximate location)

Possible Fuel Line Connection Routes

Proposed JP-8 Tank Relocation Site

Mo-gas Tanks

Helo Pads

Existing JP-8 Tanks

Incinerator

Proposed Day-Use Fuel Storage

Contour interval: 3 metres

METRES

0   100   200

N

- Mt Erebus produces high quantities of lead. Article from 1960's may provide base line data to compare sample levels to.

Collection: 18 samples collected 10/2/1999 from Scott Base and Mac Murdo.
2 more taken on 11/2/1999 at Mac Murdo at Derelict Junction and former Nuclear Reactor sight.

Sample labells.
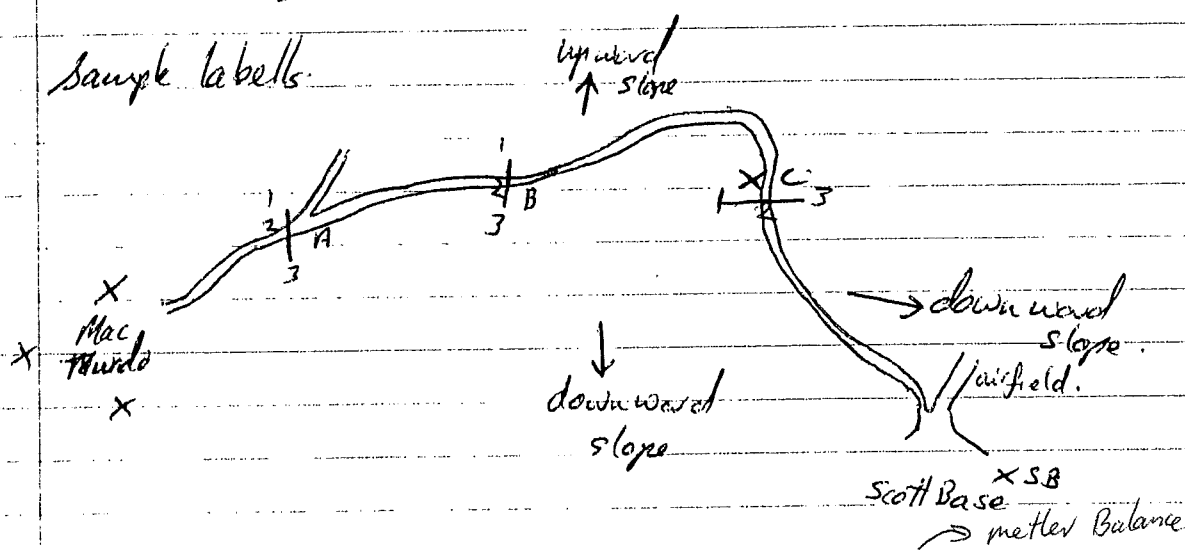
Sample	Collection site	Weight	Vol (ml)
Scott Base	car park (SB)	5.3190 g	25
Control	Black Island (BI)	5.1736 g	
C	1 up hill slope	5.2348 g	
	2 middle of road	5.5506 g	
	3 down hill slope	5.2600 g	
B	1	4.9802 g	
	2	5.2111 g	
	3	4.9553 g	
A	1	5.1007 g	
	2	5.4540 g	
	3	5.2175 g	
Mac Murdo	Return Soil (MT)	5.061 g	
Junction	(Junc)	5.1284 g	
Nuc site	(NP)	5.0290 g	

11 sample extraction were carried out on the 12/2
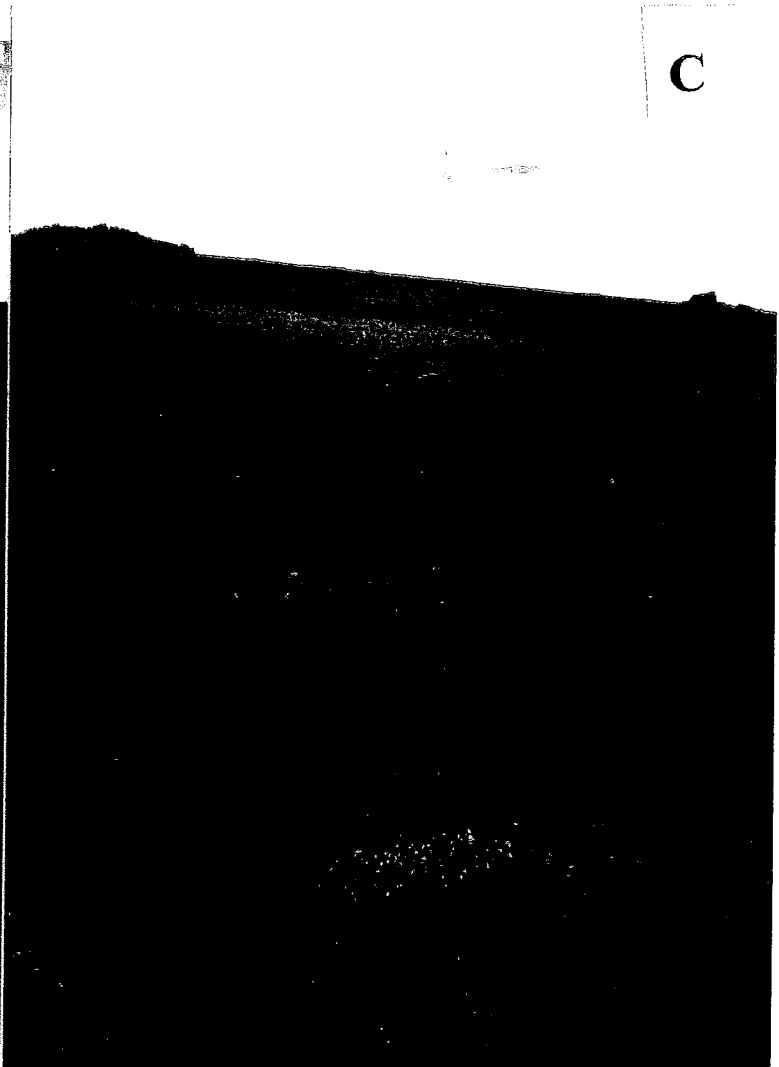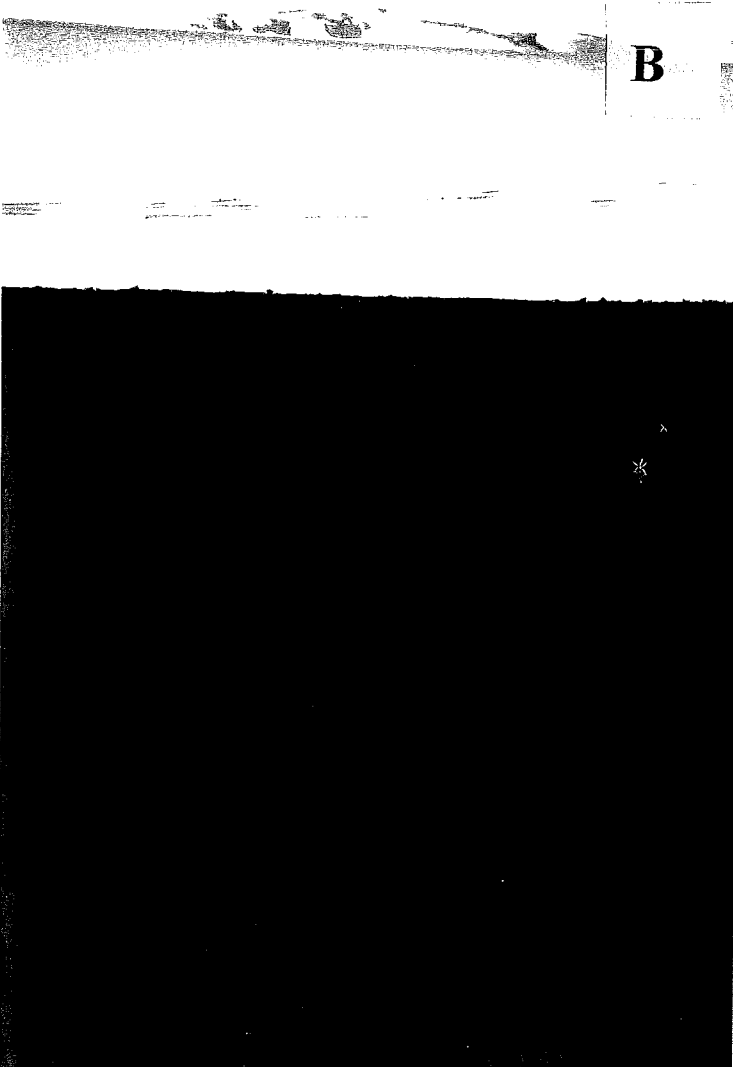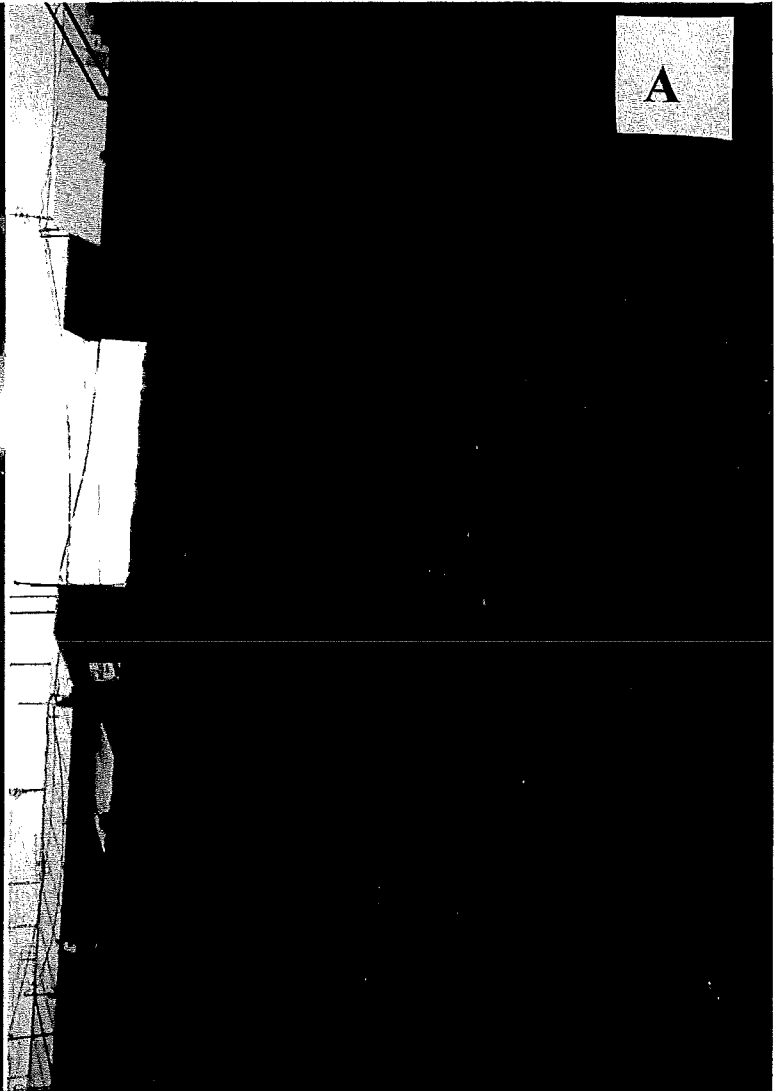
.d between Scott Base and McMurdo where soil was taken

SB

JUNC

NP
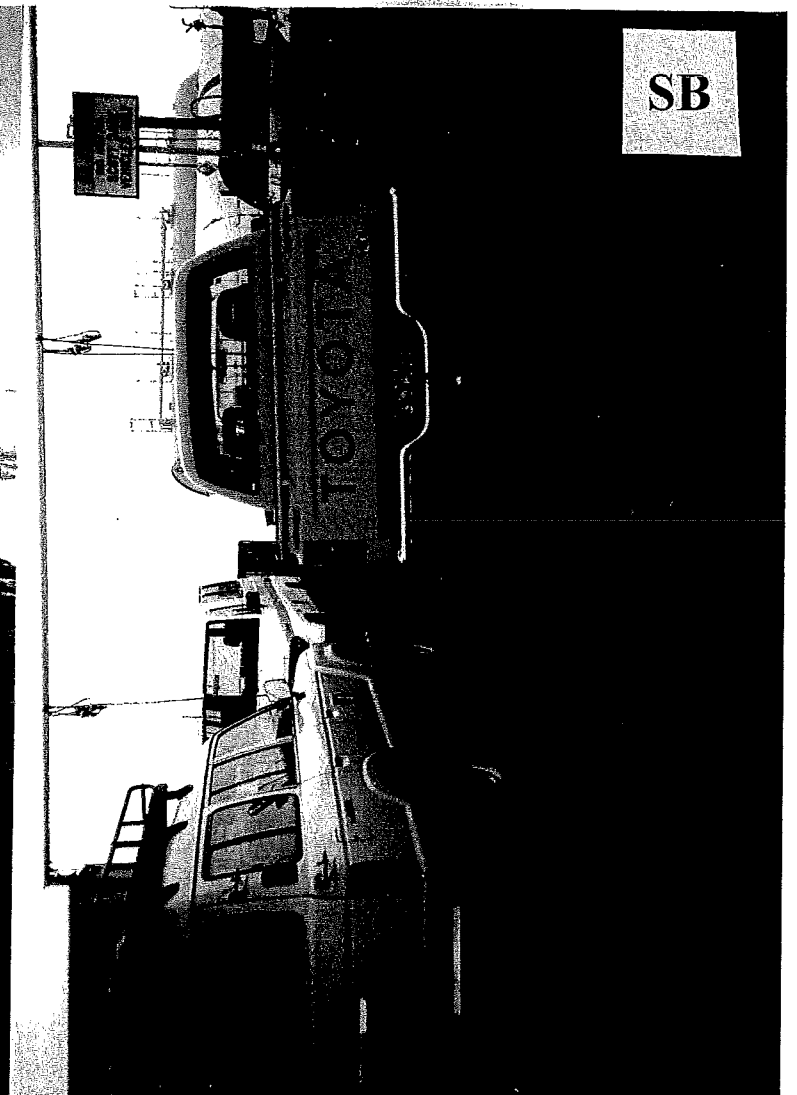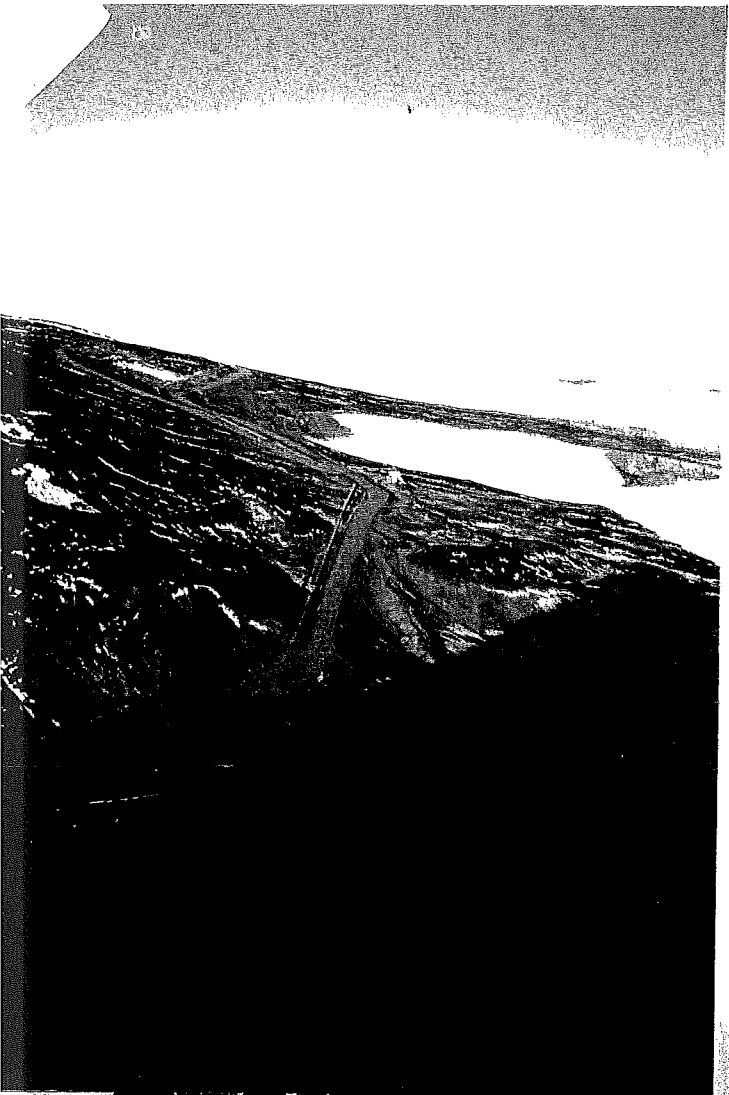
and the remaining 2 extracted on the 13/2. Following this all the samples were packed and made ready for their return to Christchurch.

15/2/99. Note: SPS pumped from MacMurdo to Williams Airfield in pipes which occationally leak. Now being welded between joint but would be interesting to check Pb levels under each joint, conc^n other heavy metals etc.

Samples returned to Christchurch Thursday 18th Feb 1999
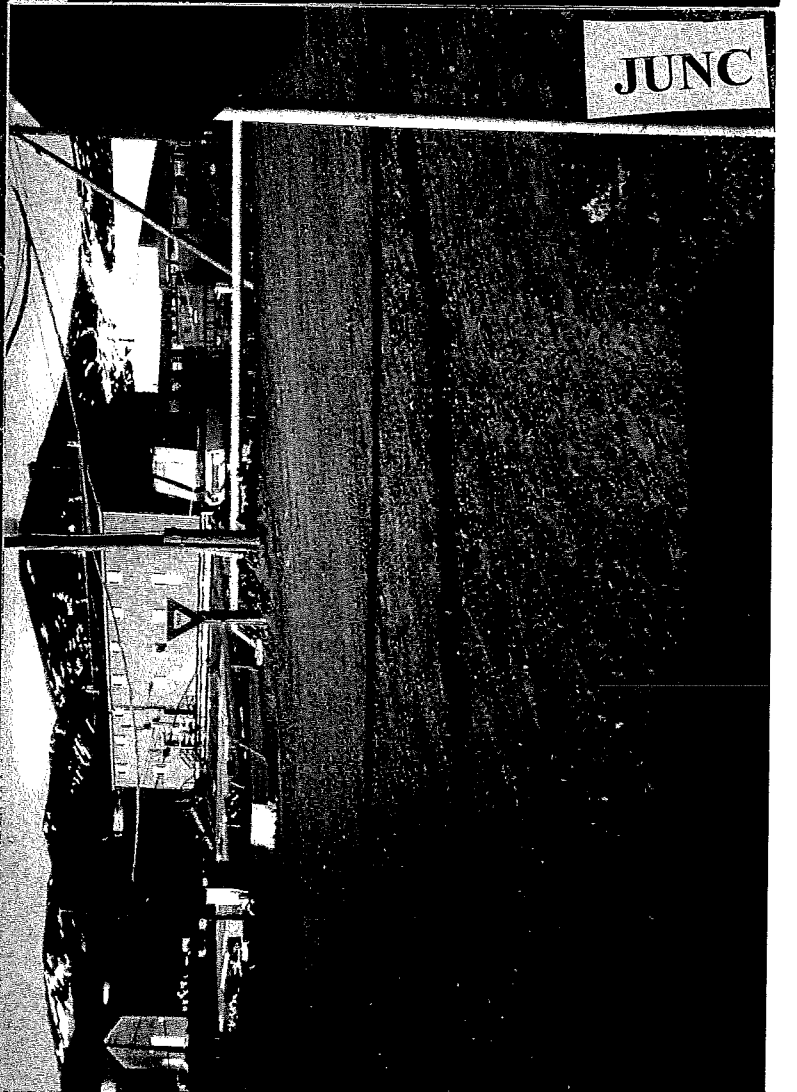
* Atomic Absorbance Spectroscopy.
  - Electrothermal
  - Flame

Require a standard to develop a calibration curve + thus determine the concentration of the samples returned.
  Use the less accurate and high conc^n electro flame AAS. If two test samples appear low on this apparatu then require Electrothermal AAS. If they appear high on the curve then samples require dilutio

Standard Preparation - (2 varing conc^n)
  Cd   0.4ppm , 0.8 ppm
  Zn   1 ppm , 2 ppm
  Pb   5ppm , 10ppm

Working Stock.
    Stocks : Pb solution ; 1000ppm
        Cd solution ; 1000ppm
        Zn solution ; 1000ppm

Add to a 500ml Volumetric flask 1ml conc^tor HNO_3 and 2ml of Cd soln (1000ppm) and 5ml Zn (1000ppm). Respectively giving 4ppm Cd and 10ppm Zn. This is Cd/Zn soln. Pb soln is at right concentration.

Three solutions to calculate calibration curve.

(a) 1ml aristar HNO_3 in 50ml Volumetric flask (made up with 49ml of MilliQ H_2O)

(b) 1ml HNO_3, plus 5ml Cd/Zn soln and 5ml Pb soln.

(c) 1ml HNO_3, plus 10ml Cd/Zn soln and 10ml Pb soln.

Preliminary Results.

Standards:

	Abs.	PPM
A	0	
B	0.267	
C	0.443	

Samples — BI (road sample)
— MT (soil returned to USA)

Pb^{+2}	Abs	ppm	dil
BI	0.027	4	$\frac{1}{2}$
MT	0.043	2	$\frac{1}{2}$

Zn^{+2}	Abs	PPM
BI	326·91	
MT	355.	

— BI used as an "average" of road sample
— MT (known to be contaminated) was an "exstream"
where do they lie with respect to cal. curve?

<u>Initial examination indicates</u> lead levels low but Zinc levels <u>high</u>. Contamination appears minimal.

<u>Back-ground correction not made</u>. Therefore require MT and BI to be re-tested. Background corr. NaCl peak.

/3 Flame AAS did not provide accurate enough results due to mechanical problems.
Electrothermal AAS was ~~thus~~ considered. The only problem is that a <u>high</u> dilution factor would be required as the machine only deals in ppb levels.

Location :- Clean room.
Preliminary Studies :- Using BI and MT. preliminary study

...xample of lead 'printout'

...stem Type	Furnace
...ement	Pb
...trix	thermal
...mp Current (mA)	4.0
...velength (nm)	283.3
...it Width (nm)	0.5
...it Height	Reduced
...strument Mode	Absorbance BC on
...mpling Mode	Auto Sampling

Graphite Furnace Parameters

...tep	Final Temp. (C)	Ramp Time (s)	Hold Time (s)	Gas Type	Read	Signal Graphics
...tep 1	90	1.0	0.0	Inert	Off	Off
...tep 2	120	20.0	20.0	Inert	Off	Off
...tep 3	150	5.0	5.0	Inert	Off	Off
...tep 4	600	10.0	5.0	Inert	Off	Off
...tep 5	400	3.6	10.0	None	Off	Off
...tep 6	2300	1.0	2.0	None	On	On
...tep 7	2300	0.1	2.0	Inert	Off	Off

Furnace Sampler Parameters

...andards Preparation	Auto-Mixed
...ple Injections	1
...ect Before Step No.	1
...ple Dry To Step No.	1
...ection Speed	4 (ul/s)
...alibration Rate	15
...ple Rate	10

Auto Mix Sampler Volumes

Sample Type	Blank Volume	Std. Volume	Sample Volume	Modifier Volume
Sample	0	0	20	10
Blank	20	0	0	10
Std. 1	15	5	0	10
Std. 2	10	10	0	10
Std. 3	5	15	0	10
Std. 4	0	20	0	10

Data Collection Parameters

Read Time (s)	3.0
Time Constant (s)	0.0
Expansion Factor	1

Program No. 1   7:27:39 am   26-Feb-1999
Calibration Mode Concentration   Measurement Mode Peak Height
Starting Recal Pb thermal

Sample Type	Conc. ug/L	%RSD	Mean Abs.	Replicates
Blank	0.000	-------	0.413	0.413

Lead levels
Modifier: Pd

Standard: (auto mix) using 50 ppb

Sample	Location	Code	Repeats	Dil. Fac	Atomic Absorbance Data			Dil Factor in Account	
					Absorbance	%RSD	Concn (ppb)	Dil. factors	Concn
1	Black Isl.	C	2		0.451	2.2	29.091	20	2.8
2	Road	A1	2		0.593	0.49	42.424	20	4.2
3		A2	2		0.27	1.31	14.858	20	1.4
4		A3	2		0.327	1.97	18.905	20	1.8
5		B1	2		0.366	2.61	21.984	20	2.2
6		B2	2		0.292	3.54	16.351	20	1.6
7		B3	2		0.345	1.25	20.279	20	2
8		C1	2		0.591	0.41	42.186	20	4
9		C2	2		0.38	2.36	22.753	20	2.1
10		C3	2		0.478	1.12	30.614	20	2.9
11	Scott Base	SB	2	D=0.10	0.325	1.39	197.448	20	18.6
12	Nuclear Pl.	NP	2		0.677	1.83	51.217	20	5.1
13	Return soil	MT	2	D=0.10	0.508	3.57	348.04	100	171.9
14	Mc. Junction	Junc	2	D=0.25	0.543	3.19	153.125	20	14.9

further dil factors by machines

$\mu g/l$

Sample dil. factors we used.

$\mu g/g$ ⇐ standard units

Cadmium levels
Modifier Pd

Standard: (auto mix) using 10 ppb Cd

Samples	Location	Code	Repeats	Dil. Fact	Atomic Absorbance Data			Dil. Factor in Account	
					Absorbance	%RSD	Concn (ppb)	Dil Fact	Concn
1	Black Isl	C	2		0.172	2.26	0.697	20	0.07
2	Road	A1	2		0.21	6.5	0.85	20	0.08
3		A2	2		0.141	3.91	0.572	20	0.05
4		A3	2		0.168	0.97	0.679	20	0.07
5		B1	2		0.199	2.88	0.806	20	0.08
6		B2	2		0.195	1.84	0.792	20	0.08
7		B3	2		0.219	1.58	0.886	20	0.09
8		C1	2		0.207	3.79	0.839	20	0.08
9		C2	2		0.166	2	0.673	20	0.06
10		C3	2		0.196	2.12	0.796	20	0.08
11	Scott Base	SB	2		0.391	1.28	2.118	20	0.2
12	Nuclear Pl.	Nuc	2		0.325	1.37	1.501	20	0.15
13	Return Soil	MT	2		0.065	3.29	1.22	100	0.6
14	Mc Junction	Junc	2		0.403	1.47	2.219	20	0.22

Zinc Levels
Modifier: 100 ppb Pd, 5% HNO

Standard: (Auto Mix) using 2ppb Zn soln

CONFIDENTIAL

Samples	Location	Code	Atomic Absorbance Data					Dil. Factor in Account	
			Repeats	Dil Factor	Absorbance	%RSD	Concn (g/b)	Dil Factor	Concn
1	Black Isl.	C	3	D=0.5	0.369	2.87	3.487	200	3.4
2	Road	A1	3	D=0.25	0.26	2.91	5.174	200	5.1
3		A2	3		0.41	2.72	1.908	200	1.7
4		A3	3	D=0.5	0.387	2.07	3.633	200	3.5
5		B1	3	D=0.25	0.345	1.8	6.565	200	6.6
6		B2	3	D=0.5	0.4	1.2	3.735	200	3.6
7		B3	3	D=0.5	0.443	1.08	4.076	200	4.1
8		C1	3	D=0.5	0.381	1.57	3.583	200	3.4
9		C2	3	D=0.5	0.328	1.15	3.14	200	2.8
10		C3	3		0.509	1.21	1.398	200	1.3
11	Scott Base	SB	3		0.83	1.23	2.129	200	2
12	Nuclear Pl.	NP	3		0.709	3.01	1.859	200	1.8
13	Return Soil	MT	3	D=0.05	0.712	3.13	37.315	1000	184.4
14	Mc Junction	Junc	3		0.608	0.9	1.627	200	1.6

* Sample Tests:

Lead: Programme: Results File 120399 Graph file: Mark 1239.
Calibration curve constructed by 'auto dilution'
series by the AAS programme.
Standard used: 50 ppb (ug/L) Modifier: Pd 20ppb 10ul
  Calibration curve: straight. Good direct proportional
    relationship between Absorbance ed concentration
Samples diluted: 50ul in 1ml ⟹ 20 fold dil. (all but MMsoil)
          + 1% HNO₃   MM diluted 100 fold
                                              10ul in 1ml.

Samples (Turn table)	Code	Repeats		Mean	% RSD	Conc" (ug/L = ppb)
1	Black Isl.	2		0.451	2.20	29.091
2	A1	2		0.593	0.49	42.424
3	A2	2		0.270	1.31	14.858
4	A3	2		0.327	1.97	18.905
5	B1	2		0.366	2.61	21.984
6	B2	2		0.292	3.54	16.351
7	B3	2		0.345	1.25	20.279
8	C1	2		0.591	0.41	42.186
9	C2	2		0.380	2.36	22.753
10	C3	2		0.478	1.12	30.614
11	Scott Base	2	D=0.10	0.325	1.39	197.448
12	Nuc. Plant	2		0.677	1.83	51.217
13	Soil from MM (MT)	2	D=0.10	0.508	3.57	348.040
14	MM Junction	2	D=0.25	0.543	3.19	153.125

(refer to result table   Dil factors by AAS taken into account for ug/L
ad 3rd page)   Value

Note: Samples from Scott Base, MM Junction, ed MM soil (MT) were further
  diluted by the AAS so they would appear on
  the calibration scale.
    Therefore SB, MM Junction ed MM soil all have high levels
  of lead present in the soil collected. Due to the
  dilution by the machine, it would be more accurate
  to make a sample with a higher vol. of the original
  sample at the dilution made by the machine.
    Therefore in the future SB, MM Junction ed MM soil
  will be re-tested.

Cadmium : Results file : 12039913 : Graphfile : Mard 1293
Calibration curve created by 'auto dilution' programme
by AAS

Standard : Cd 10ppb   Modifier : Pd 20ppb, 10ul

Calibration curve - slightly curved (try to avoid this)
curve not too pronounced - it was the best
calibration curve created by our programme

I present an extract from the printout of the Cd
test.

Sample Dillution : 50ul in 1ml.
                        + 1% HNO₃

Instrument Parameters

System Type   Furnace
Element   Cd
Matrix   thermal
Lamp Current (mA)   3.0
Wavelength (nm)   228.8
Slit Width (nm)   0.5
Slit Height   Reduced
Instrument Mode   Absorbance BC on
Sampling Mode   Auto Sampling

Graphite Furnace Parameters

Step	Final Temp. (C)	Ramp Time (s)	Hold Time (s)	Gas Type	Read	Signal Graphics
Step 1	90	1.0	0.0	Inert	Off	Off
Step 2	120	20.0	20.0	Inert	Off	Off
Step 3	150	5.0	5.0	Inert	Off	Off
Step 4	600	10.0	5.0	Inert	Off	Off
Step 5	400	3.6	10.0	None	Off	Off
Step 6	2300	1.0	2.0	None	On	On
Step 7	2300	0.1	2.0	Inert	Off	Off

Furnace Sampler Parameters

Standards Preparation   Auto-Mixed
Sample Injections   1
Inject Before Step No.   1
Sample Dry To Step No.   1
Injection Speed   4 (ul/s)
Recalibration Rate   15
Rescale Rate   10
Rescale Std. No.   3

Auto Mix Sampler Volumes

Sample Type	Blank Volume	Std. Volume	Sample Volume	Modifier Volume
Sample	0	0	20	10
Blank	20	0	0	10
Std. 1	16	4	0	10
Std. 2	12	8	0	10
Std. 3	8	12	0	10
Std. 4	0	20	0	10

Data Collection Parameters

Read Time (s)	3.0
Time Constant (s)	0.0
Expansion Factor	1

Program No. 1   6:39:58 am   3-Mar-1999
Calibration Mode Concentration   Measurement Mode Peak Height
Starting Recal Cd thermal

Sample Type	Conc. ug/L (ppb)	%RSD	Mean Abs.	Replicates	
Blank	0.000	-----	0.024	0.024	0.023
Standard 1	1.000	1.49	0.247	0.249	0.244
Standard 2	2.000	0.79	0.367	0.369	0.365
Standard 3	3.000	1.67	0.465	0.470	0.459
Standard 4	5.000	0.42	0.617	0.619	0.615

Concentration

CONCENTRATION OF Cd ug/L
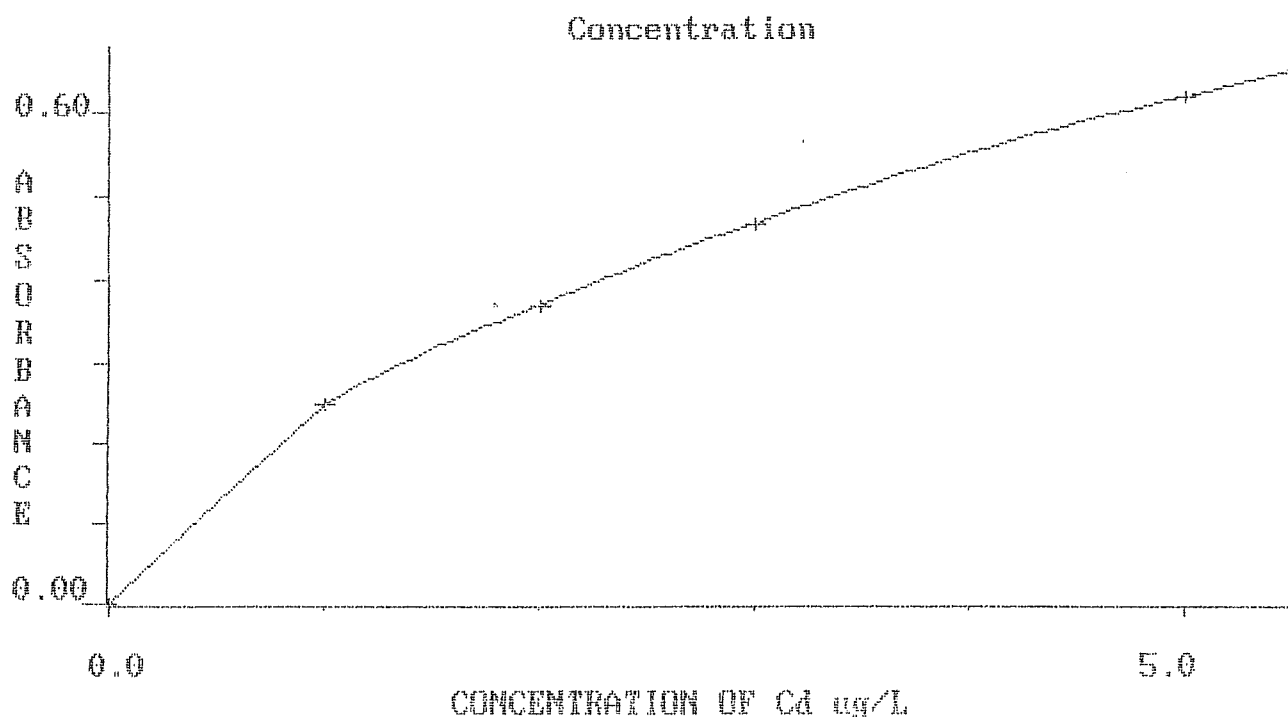
Have to work on this for final results.

Sample Type	Conc. ug/L	%RSD	Mean Abs.	Replicates	
sample 1	0.697	2.26	0.172	0.175	0.169
sample 2	0.850	6.50	0.210	0.200	0.219
sample 3	0.572	3.91	0.141	0.137	0.145
sample 4	0.679	0.97	0.168	0.169	0.166
sample 5	0.806	2.88	0.199	0.195	0.203
sample 6	0.792	1.84	0.195	0.198	0.193
sample 7	0.886	1.58	0.219	0.216	0.221
sample 8	0.839	3.79	0.207	0.213	0.202
sample 9	0.673	2.00	0.166	0.169	0.164
sample 10	0.796	2.12	0.196	0.199	0.193

Rescale Cd thermal

Sample Type	Conc. ug/L	%RSD	Mean Abs.	Replicates	
Rescale-Blank	0.000	------	0.020	0.020	0.021
Rescale-Std. 3	3.000	0.12	0.478	0.479	0.478
sample 11	2.118	1.28	0.391	0.395	0.388
sample 12	1.501	1.37	0.325	0.322	0.328
sample 13	0.254	3.29	0.065	0.066	0.063
sample 14	2.219	1.47	0.403	0.399	0.407
sample 15	0.585	0.52	0.148	0.149	0.148

Recal Cd thermal

Sample Type	Conc. ug/L	%RSD	Mean Abs.	Replicates	
Blank	0.000	------	0.021	0.019	0.023
Standard 1	1.000	4.95	0.247	0.238	0.256
Standard 2	2.000	2.83	0.380	0.372	0.387
Standard 3	3.000	1.37	0.480	0.485	0.475
Standard 4	5.000	1.98	0.626	0.635	0.618

Sample Type	Conc. ug/L	%RSD	Mean Abs.	Replicates	
sample 16	1.220	0.85	0.283	0.284	0.281

Background Correction
- space NaCl & sample peaks
- use Pd modifier.

(NaCl & sample peaks) must separate

split sample peak and NaCl (background)

| 26.56 TIME | PROGRAM 1 OVERVIEW | 1.00 secs/div MARK1293 | sample 2 REPLICATE 2 | 46.40 TIME |
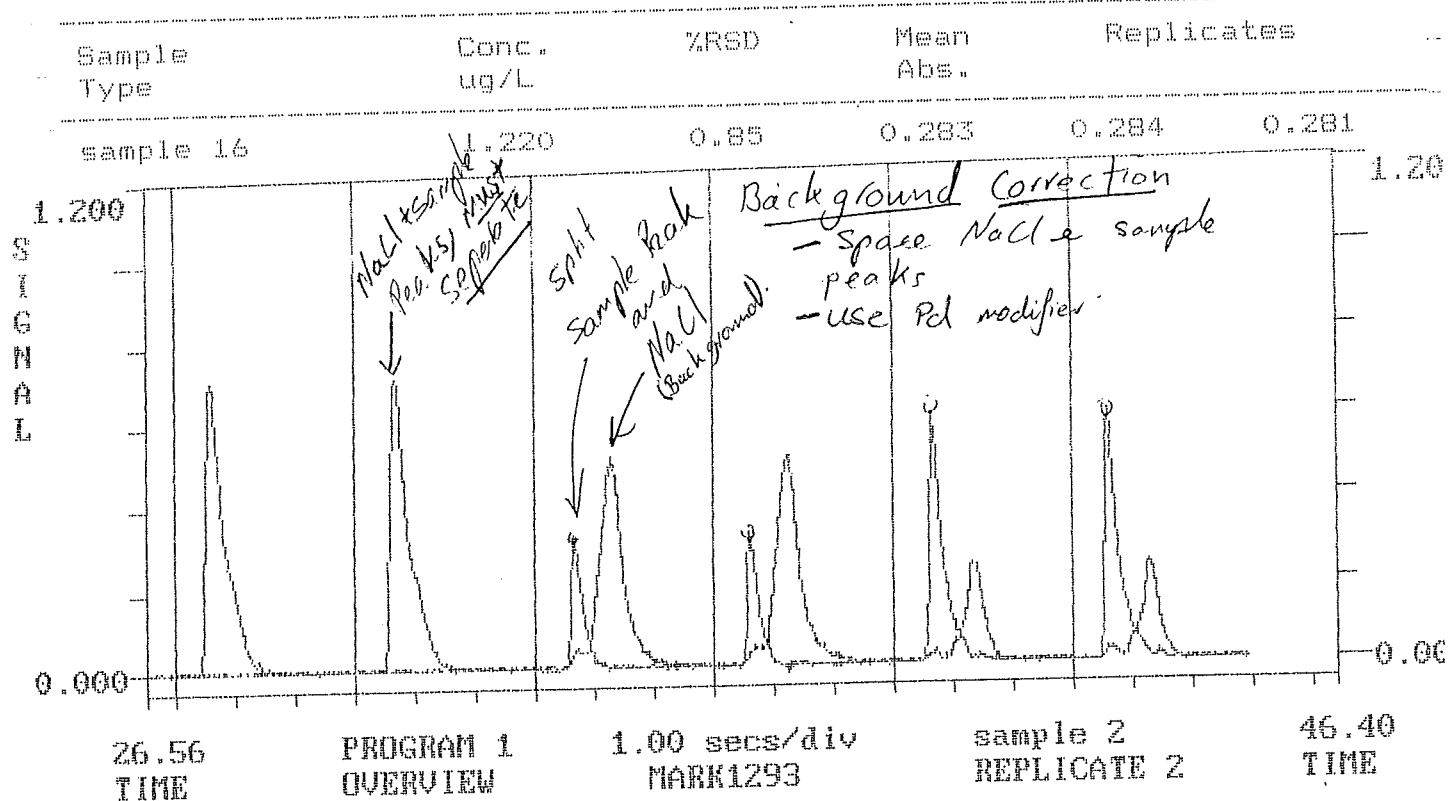
Zinc:

Calibration curve created by 'auto dilution' programme by AAS. Straight calibration curve.

Standard: Zn 2ppb

Modifier: Pd 100ppm   5% HNO_3.

Zn levels very high. AAS very sensitive to its presence. Sample dilution: 50ul in 1ml, 8ul of this was diluted in 800ul of MilliQ H_2O (Dil. Factor ≈ 200)

Samples	Code	Repeat		Mean	% RSD	Conc^n (ug/L)
1	C	3	D=0.5	0.369	2.87	3.487
2	A1	3	D=0.25	0.26	2.41	5.174
3	A2	3		0.41	2.72	1.908
4	A3	3	D=0.5	0.387	2.07	3.633
5	B1	3	D=0.25	0.345	1.8	6.565
6	B2	3	D=0.5	0.4	1.2	3.735
7	B3	3	D=0.5	0.443	1.08	4.076
8	C1	3	D=0.5	0.381	1.57	3.583
9	C2	3	D=0.5	0.328	1.15	3.14
10	C3	3		0.509	1.21	1.398
11	SB	3		0.83	1.23	2.129
12	NP	3		0.709	3.01	1.859
13	MT	3	D=0.5	0.712	3.13	37.315
14	June	3		0.608	0.9	1.627

Note: for _ug/g_ values refer to spread sheet Data (standard units).

_ug/L_ x Dil factor we made.

$$ug/g = \frac{ug/L \times Vol. \left(\frac{ml}{1000}\right)}{soil (g)}$$

Vol = 25ml ⇒ 0.025L
soil taken = ~5g

refer to 3rd page

Initial review of Results:

- Lead results appear to be high in regions of concentrated human activity, with Scott Base and Mac Murdo (soil return) having highest levels. Due to high dilution factors used by the auto dilution of the AAS, it would be wise to retest these high samples at a greater volume / greater dilution involving new samples.

Road samples appear to lie in similar magnitude to the control (Black Island) Therefore it is impossible to relate road lead levels to human activities. Tentitively it appears:

above road > bottom of road > middle of road (traffic)

It would be logical that machinery / would push deposits to sides of road.

Of all test Pb results appear to be most interesting and relevant.

- Cadmium results indicate tiny levels of Cd. Road levels appear to lie within Black Island Control. Presence of Cd at Black Island can only be explained by the presence of naturally occuring residual levels or prehapes a release of Cd from the plastic sampling containers used in the process (Personal Correspondence Managing Director of NZ Radiation Laboritories).

Areas of human habitation shows slightly higher levels, but not of an extent that I believe is significant.

These results I believe give merit to the claim that contamination was minimal. As the base line is relatively constant (Average of road samples) It rises in regions where lead appeared high, but not to any significant concentration. max 0.6ug/g (Therefore contamination by me or lab at Scott Base was low, if at all).

- Zinc levels were significantly harder to test.
Naturally occuring zinc levels are very high.
Electrothermal techniques works in units of ppb (ug/L)
The level of lead was too high to fit within this
scale and dilution by us of 200 fold were followed
by AAS dilution of up to $p=0.05$ (95%)
    Significantly high levels were again seen in the
McMurdo (return soil) sample, but this is prehapes the
only correlation to the Pb and Cd tests.
    Any future studies on Zn levels would be encouraged
to use a Flame AAS as natural abundance is very high.

Observations from Initial Examination.
    Areas of concentrated human activity at Scott Base and
McMurdo Station show a minimal level of heavy
metal contamination. These sites include, the scott Base
car park and the McMurdo mainstreet junction. Lead levels are of
the most significance meant also a minimal residual natural level of
lead is apparent as indicated by Black Island Sample.
    Cadmium level are low throughout all areas tested.
A residual level is apparent however. (natural level) possible
produced from volcanic activities.
    Likewise the high level of zinc found appears to be from
natural sources. (volcanic activity and the like) Both Cadmium
and zinc levels are only effected by human activity in the
McMurdo (return soil) samples. which was known to contain
high levels of heavy metal contamination.
    Road sampling did not indicate solid trends. It
would appear that taking soil from greater depths in
the road may produce more interesting results.
In Antarctica heavy metals do not move down the soil
column but remain on the surface where they are deposited.
Due to grading of the road after every season, it
would seem layers may be built up under the road
(stratified)

Standards:
50ul sample, 10ul with 20ppb Pd soln as a modifier for Cd cd Lb tests.
   Due to high levels of NaCl in the solutions a modifier must be added. The marine environment where the samples were collected, ~~it~~ plus the summer evaporation where water brings salts through the soil to the surface ~~during summer~~ give these high NaCl levels.
   Other salts are present in the 'back ground' but not to significant levels.

					In	Pd	Cd
Sample 1.	Pb	Bl.	read	50ul	1ml	Okay	Okg
Sample 2.		MT	conc^n	10ul	1ml	?	Okg

Standard 1 = 37.5ppb   Standard 3 = 12.5ppb
Standard 2 = 25.0ppb   Standard 4 = 0.9ppb

Within range.
thus have right
conc^n ~~dilution~~

Pb level 5ul — A = 0.60 (cf A = 0.42).

Principles of Atomic Absorption

1.1.1 Atomic Spectra

In 1900, Max Planck established the quantum law of radiation absorption and emission. The quantum law states that atoms can only absorb radiation of a well-defined wavelength λ; i.e. they can only take up and release definite amounts of energy E. The relationship between the energy transition and the wavelength, where h is Planck's constant, ν the frequency, and c the speed of light, is expressed as follows:

$$E = h\nu = \frac{hc}{\lambda} \qquad (1.1)$$

Upon absorbing a quantum of energy, an atom enters an "excited" state. When the atom returns to a lower energy state, it releases the absorbed energy; usually as radiation. Because atoms can exist in many different excited states, many energy transitions are possible. Radiation is emitted at discrete wavelengths, each corresponding to a different energy transition. For atoms that are excited thermally or electrically, absorbed energy can be released as an emission spectrum. If the excitation is by optical radiation, an absorption line-spectrum is observed. Absorption spectra have fewer lines than emission spectra because in an absorption spectrum virtually all lines must come from transitions originating from the ground state. These absorption lines are referred to as resonance lines since they come into resonance with optical radiation of suitable frequency. For any element, the resonance lines in the absorption spectrum will be common to the emission spectrum. These common lines form the basis of atomic absorption spectrometry (AAS).

Because all elemental absorption spectra are different, it is possible to select resonance lines unique to one element. Hence, from a mixture of gaseous atomic species placed in the path of a radiation source, an element can be selectively determined by measuring the radiation attenuation at this element's resonance line.

1.1.2 Absorbance

The phenomenon of light absorption has been studied for over 200 years. In 1760, Lambert set the theoretical foundations of modern absorption spectrophotometry when he expressed the relationship between incident light intensity I_o, and the transmitted light intensity I_{tr}, for light passing though a layer of thickness l. The absorption coefficient x' measures the layer's light attenuating power.

$$I_{tr} = I_o.e^{-x'l} \qquad (1.2)$$

When the absorber is a solution of an absorbing substance in a non-absorbing medium, the absorption coefficient is proportional to the concentration c. The proportionality constant ε is known as the molar absorptivity of the absorbing substance.

$$x' = \varepsilon.c \qquad (1.3)$$

Lambert's law was thoroughly examined by Beer in 1852, and re-written to state that absorbance (A) is proportional to the concentration of the absorbing substance, and to the thickness of the absorbing layer. This expression is now known as the Beer-Lambert law. It is usually used in atomic absorption spectrometry in the following form:

$$A = \log\frac{I_o}{I_{tr}} = \varepsilon.N_0.l \qquad (1.4)$$

where N_0 is the number of absorbing (i.e. ground state) atoms in the radiation path. If the absorbing atoms are produced from an element in solution, N_0 is proportional to the element's solution concentration.

1.1.3 Atomic Absorption Spectrometry

In 1955, independent publications by Walsh,[1] and Alkemade and Milatz[2] recommended atomic absorption spectrometry as a generally applicable analytical method which combines the selectivity of atomic absorption and the linearity of the concentration-absorbance relationship. In subsequent years, it was principally Walsh and his CSIRO[*] coworkers who developed atomic absorption into a sensitive and highly selective analytical method. The atomic absorption spectrometers developed by the early AAS researchers contained the same basic features that are now found in modern instruments (Figure 1.1).

1.1.4 Atomic Absorption Instrumentation

The essential parts of an atomic absorption spectrometer are a radiation source, an absorbance cell/atomiser, a monochromator, and a detector which is connected to an amplifier and a recording device.

Radiation Sources: The specificity of AAS is largely due to the narrow width of the resonance lines and the fact that elemental absorption takes place over a very narrow spectral range. The ideal radiation source for AAS would provide high intensity, extremely narrow emission lines. The most commonly used elemental emission source is the hollow cathode lamp (HCL). This uses an electric discharge between an anode and an elemental cathode to ionise an inert gas. The gas cation then strikes the cathode surface, dislodging atoms of the cathode material. Collisions with inert gas ions then excite the cathode-sourced atoms into radiating their spectral lines. Hollow cathode lamps are available for about seventy different elements, and for most, provide sufficiently intense low-noise radiation.

Radiation source   Atomiser   Monochromator   Detector   Amplifier   Recorder
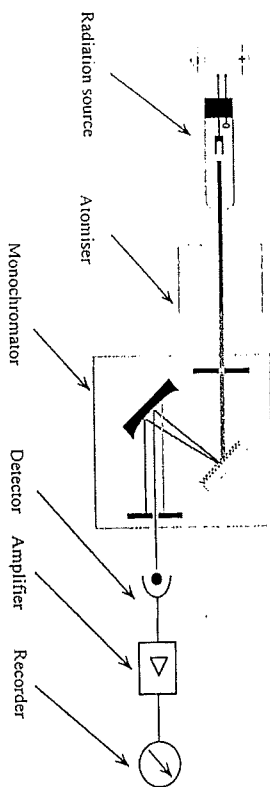
Figure 1.1 Schematic diagram of a modern atomic absorption spectrometer.

The other most common radiation source used for AAS is the electrodeless discharge lamp (EDL). This consists of a sealed quartz tube which is filled with a few milligrams of the analyte element (as pure metal, halide, or metal with added iodine) under an argon pressure of a few hundred pascal. The tube is mounted within the coil of a high frequency generator (e.g. 2400 MHz) and excited by an output from a few Watts up to 200 Watts. The filler gas forms a plasma, in which collisions with analyte vapour lead to dissociation, excitation and emission. Electrodeless discharge lamps have several advantages over hollow cathode lamps. Firstly, the emission lines are generally narrower than for hollow cathode lamps. They can be produced for all volatile elements, and they emit radiation that is orders of magnitude more intense than that emitted by hollow cathode lamps. The increased radiation intensity leads to better signal to noise ratios, and hence, better precision and lower detection limits. For some elements, especially arsenic where the detection limit is improved by an order of magnitude, electrodeless discharge lamps have almost entirely supplanted hollow cathode lamps.[3]

Atomisers: The analyte emission spectrum from the radiation source is passed through an atomiser which doubles as an absorption cell. Within the cell, the sample is present as atoms which are generated by thermal dissociation. The atomiser's most important function is to produce ground-state (i.e. absorbing) atoms from ionic or molecular analyte in the sample. Sensitivity is directly proportional to the degree of analyte atomisation, so depends strongly on atomisation efficiency. The original atomising technique used by Alkemade and Milatz[2] was to spray the sample solution into a flame using a nebuliser. This technique is still widely used, but has since been joined by others; the hydride, cold vapour and graphite furnace techniques.

It is necessary to eliminate interfering radiation emitted by the hot atomiser (flame etc). This is achieved by pulsing the output of the radiation source. The detector then receives two types of signal; an alternating one from the radiation source, and a constant one from the atomiser. An electronic filter is used to remove the constant signal, passing only the alternating signal from the radiation source to the amplifier.

Monochromators: After passing through the atomised sample, radiation passes through a monochromator before reaching the detector. The monochromator's main purpose is to separate the analytical resonance line from the many emission lines produced by the source. Another is to reject radiation generated by flame emission or by the heated graphite furnace. Light passes into the monochromator through an entrance slit, and is focused onto a diffraction grating by a collimator mirror. Radiation falling onto the grating is reflected and dispersed in a wavelength dependent arc, a portion of which is reflected by a camera mirror and passed through a variable exit slit. Depending on the type of diffraction grating used, and the width of the exit slit, monochromators can resolve a bandpass of 0.05 to 10 nm.[4] For practical purposes, a bandpass of 0.2 to 2.0 nm is sufficient to adequately resolve most elemental resonance lines.

Detectors, Amplifiers and Recorders: Radiation passing through the monochromator exit slit is measured using a photomultiplier tube. The resulting signal is then amplified and fed to a recording device. In early instruments this comprised an analog gauge and/or a chart recorder. Modern instruments generally use a dedicated microcomputer that is also used for controlling instrumental parameters and for data manipulation.

The flame atomiser-AAS used by Walsh,[1] and Alkemade and Milatz[2] is now established as a routine procedure in all branches of inorganic elemental analysis. For most metals, possible interferences are well known, and easily controlled.[5] Analysis in the mg L^{-1} (ppm) range is highly reproducible for many elements, and with quality instruments, precision of 0.2% RSD can be achieved.[6]

1.2 ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

1.2.1 The Graphite Furnace Atomiser

The search for enhanced detection limits in AAS led L'vov to conceive the graphite furnace.[7] The flame atomiser is inefficient for two main reasons. Firstly, the nebuliser introduces only 1-15% of the sample solution into the flame.[3] Secondly, because of the flame's burning velocity, sample atoms are rapidly swept out of incident radiation beam. These two inefficiencies serve to limit the number of atoms in the light path at any one time, hence lowering sensitivity. L'vov sought to eliminate both of the flame's inefficiencies by using a heated graphite tube as an atomiser. In L'vov's apparatus, the graphite tube was mounted so that the beam from a hollow cathode lamp passed through tube's centre. The sample was dried onto the tip of a carbon electrode which was then inserted through a hole into the graphite tube. The sample was atomised by a dc arc and the transient atomic absorbance recorded. In this system the entire sample volatilises and most is atomised, thus removing nebuliser inefficiencies. In addition, the residence time of the sample atoms in the radiation beam is greatly increased. With an improved version of this atomiser, L'vov obtained absolute detection limits between 10^{-10} g and 10^{-14} g; better by several orders of magnitude than the limits of flame-AAS.[8] Following L'vov's early work, Massman proposed a much simpler

method for graphite furnace atomisation.[9] In Massman's system, 50 µL of sample was introduced into a 5 cm long graphite tube through a small hole in the tube wall. The tube was then heated resistively by passing a high current (500 A) at low voltage (10 V) through it. This resistance heating permitted fine temperature control, so optimum atomisation conditions could be selected for each element. The Massman furnace was constantly purged by a stream of argon to prevent atmospheric oxygen from oxidising the tube. This gas purging reduced the residence time of atoms in the tube, and led to detection limits an order of magnitude poorer than those obtained by L'vov. Also, Massman's atomisation time was longer because the resistance heating rate is slower than for L'vov's dc-arc atomisation. However, the simplicity of Massman's system led to it being used as the basis for modern graphite furnace atomisers which have now largely overcome the early system's deficiencies.

Graphite furnace atomic spectrometry is now generally referred to as electrothermal atomic absorption spectrometry (ETAAS). A modern electrothermal atomiser is the furnace. Of the many different materials that have been used as atomisers, none has been as successful as the pyrolytically coated graphite tube.[10] In order to ensure good sensitivity and reproducibility, the furnace must exhibit certain properties. Such requirements include: low porosity, chemical inertness, low levels of metal impurities, good thermal and electrical conductivity, high rigidity, high melting point, reasonable cost, good machinability, and low thermal expansion. As a furnace material, graphite satisfies many of these criteria, but does have problems with porosity and chemical inertness. By coating the furnace with a layer (ca. 30 µm thick) of pyrolytic graphite, the sample is prevented from penetrating the tube, thus reducing memory effects. The pyrolytic coating also lessens carbide formation; a problem often associated with refractory elements.

1.2.2 Graphite Furnace Operation

In principle, the graphite furnace operating protocol is simple. The furnace is clamped longitudinally between two graphite electrodes as shown in Figure 1.2. The sample is injected (usually by an autosampler) through the hole in the top of the furnace and onto the furnace wall. The furnace is then heated by passing a current between the two supporting electrodes. The furnace temperature is slowly raised to the solvent's boiling point to dry the sample ("drying" step). Then the sample is pyrolysed by raising the temperature to a point where matrix components are decomposed but the analyte is not volatilised ("pyrolysis" step).
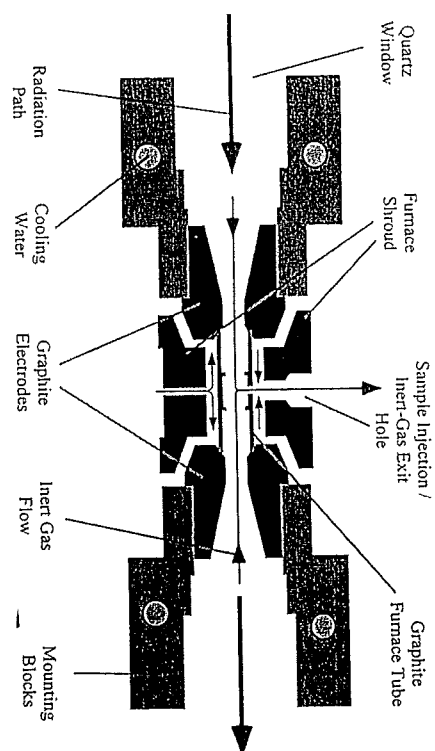

Quartz Window — Furnace Shroud — Sample Injection / Inert-Gas Exit — Graphite Furnace Tube — Hole — Radiation Path — Cooling Water — Graphite Electrodes — Inert Gas Flow — Mounting Blocks

Figure 1.2 Modern electrothermal atomiser (GBC GF3000).

When pyrolysis is complete, the furnace temperature is ramped rapidly ($>1000\ °C\ s^{-1}$) to a value where the analyte is atomised ("atomise step"). During the atomise step (three to five second duration), the absorbance is measured, and the sample concentration can be read from a calibration curve. During the drying and pyrolysis steps of the temperature program, the furnace is bathed in an inert gas (usually nitrogen or argon) to prevent atmospheric oxygen from oxidising the graphite; the inert gas flow also serves to accelerate the sample drying. In order to extend the residence time of atoms within the furnace, the inert gas flow is switched off prior to atomisation. The furnace is then allowed to equilibrate for up to ten seconds before atomising.[11] A typical temperature versus time profile for the graphite furnace is shown in Figure 1.4.
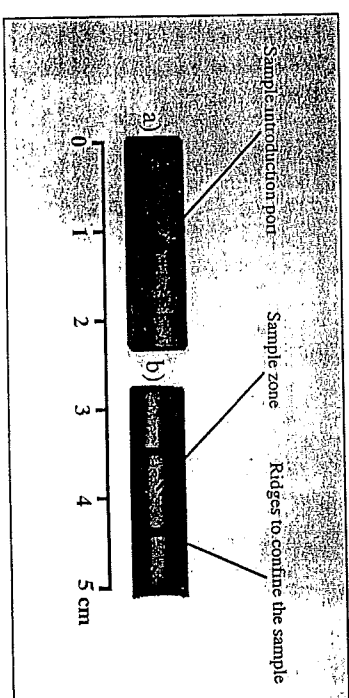

Sample introduction port — Sample zone — Ridges to confine the sample — a) — b) — 0 1 2 3 4 5 cm

Figure 1.3 A typical pyrolytic graphite-coated furnace tube: a) top view b) longitudinal cross-section.
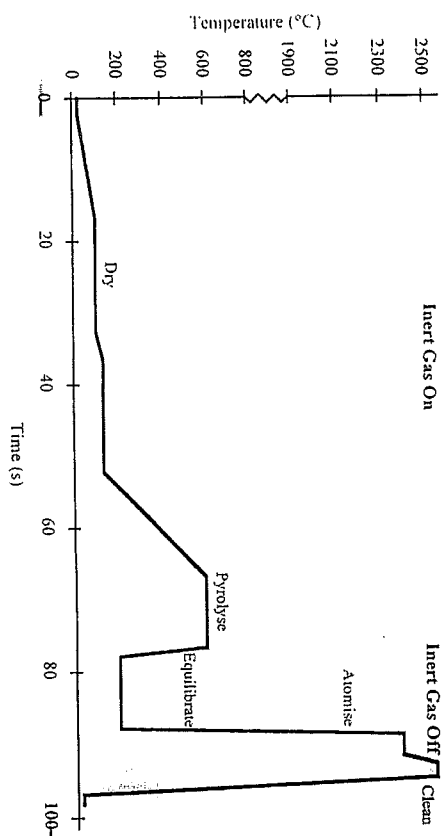
Although the operating principles for the graphite furnace atomiser are simple, there are many reasons why measurements may be inaccurate. Such inaccuracies are often associated with sample matrix components (interferents) which enhance or diminish the production of atoms, relative to aqueous standards.

1.3 INTERFERENCES IN ETAAS

Two classes of interference are encountered in ETAAS. Spectral interferences generally arise when absorption by an interfering atomic or molecular species overlaps, or lies so close to the analyte absorption that resolution by the monochromator becomes impossible. Chemical interferences result from various chemical interactions that suppress or enhance analyte volatilisation and atomisation.

1.3.1 Spectral Interferences

Various spectral interferences can be encountered in ETAAS. Most can be traced to molecular species produced by the volatilised sample matrix, however some are a direct result of overlapping spectral lines. In the latter case for example, a vanadium line at 308.211 nm interferes with an aluminium analysis at 308.215 nm. Because it is not possible to resolve such close wavelengths, the aluminium analysis is accomplished employing the 309.27 nm aluminium line instead. In addition to sample-derived interferences, emission lines from the HCL or EDL filler gas (neon or argon) may fall within the spectral bandpass of the monochromator. Such "direct spectral overlaps" are rare, and can be predicted from tables of overlapping elemental resonance lines.[4] More common and more difficult to control are the interferences caused by sample matrix components.

Figure 1.4 Typical temperature versus time profile for graphite furnace atomisation.

In ETAAS, sample matrix components cannot always be removed during the pyrolysis step. During the atomise step, any remaining components are volatilised along with the analyte. Problems arise when these components persist as molecules or particulates in the gas phase. For example, when determining lead in a sodium chloride medium, the lead is atomised and the sodium chloride volatilised at the same temperature; ca. 1100 °C. Radiation scattering by non-volatilised particles, or broad-band molecular absorption by concomitant species such as $NaCl_{(g)}$ gives rise to non-specific or background absorption.

In practice, it is difficult to differentiate the two causes of background absorption, however the same measures are taken to counter each. The first strategy is to distinguish between analyte and interferent (background) absorbances by using their differing spectral characteristics. This approach is known as background correction. The alternative strategy is to alter the sample matrix in such a way that the analyte and interfering species are no longer volatilised at the same temperature. This technique, known as chemical modification, is discussed in section 1.3.2.

1.3.1.1 Background Correction

Several different types of background correction system are used in ETAAS. All are variations on the same concept. The absorbance at the wavelength of the analytical line is the sum of the atomic absorbance and of all other interfering absorbances. If the interferent absorbance can be measured separately (eg. at another wavelength), then the atomic absorbance can be calculated by difference. The two most popular methods used to achieve this are the Continuum Source, and Zeeman background correction systems.

Continuum Source Background Correction: (ie as used in the GBC908)

Light dispersion by particulates and absorption by molecular species is generally across a broad band whereas atomic absorption is restricted to a narrow resonance line. This difference can be exploited by passing radiation from two different light sources alternately through the graphite tube atomiser. One source, a deuterium lamp, provides a continuous source of radiation across the ultraviolet spectrum (190-350 nm). The other source, an EDL or HCL provides the atomic resonance line. Because the monochromator band pass is wide relative to the resonance line, the fraction of the continuous source radiation absorbed by analyte atoms is negligible. Therefore the absorbance measured using the continuous source represents background (molecular) absorbance. The absorbance measured at the resonance line using the atomic source, represents the sum of the background and atomic absorbances. The atomic absorption is calculated by difference. This system works well within certain limits. Because the deuterium arc lamp used as a continuum radiation source has a low output in the visible region, background correction is limited to the ultraviolet (although this is where molecular absorption is prevalent). Also, if the analyte concentration is high, then the amount of continuum radiation absorbed by analyte atoms becomes significant, and may result in overcorrection. For this reason sample absorbances should be kept below 0.7 absorbance units, diluting when necessary. The continuum source method cannot

adequately compensate for highly structured background absorption. Also, it is limited to a maximum background absorbance of around 1.0 absorbance units,[3] a value easily reached, given that matrix components are often present at more than 10^6 times the analyte concentration.

1.3.2 Chemical Interferences

Chemical interferences, also known as *physical interferences*, are a major problem in ETAAS. These interferences are caused by interactions between the analyte, and the sample matrix components, furnace, or sheath gas. However, all lead directly or indirectly to a lower atomic population on atomisation and hence to decreased sensitivity.

Chemical interferences can be divided into those that originate in the condensed phase and those that originate in the vapour phase. Condensed phase interferences include:

i) Analyte losses during pyrolysis, and early volatilisation during the atomise step due to volatile compound formation.

ii) Incomplete volatilisation during the atomise step due to occlusion, or formation of refractory compounds.

iii) Processes that change the rate at which the analyte is volatilised.

Vapour phase interferences include changes in the rate at which the analyte is removed from the furnace, and formation of analyte molecular species in the gas phase. For example, reactions of analytes with oxygen, nitrogen and carbon to form oxides, nitrides and cyanides. Vapour phase interferences commonly relate to dissociation equilibria of element related components. For example, when chlorides are present during lead atomisation, $PbCl_2(g)$ occurs at temperatures below 900 °C, however $Pb(g)$ is the preferred species at temperatures above 1200 °C.[3] The rate at which the chloride is converted to the metal affects analytical sensitivity.

Many types of chemical interferences have been documented and reviewed,[3,14,15] but there is one that deserves special mention. Of all the interferences encountered in ETAAS, the most significant are those arising from chloride. The chloride ion is a common species in many media, especially in marine samples and in biological extracts and fluids. Not only is the chloride ion ubiquitous, but it directly or indirectly suppresses the analytical absorbances for many elements.[3] The mechanisms by which it does so have been the target of several recent studies.[16-18] There is a general consensus that chloride interferes through a variety of independent mechanisms. Because these are common to many other interferents, the chloride mechanisms serve to illustrate typical modes of chemical and spectral interference.

The most severe chloride interferences are observed when metals which form chlorides with low melting points (e.g. lead and cadmium) occur in chloride-containing media. During the pyrolysis stages the volatile metal chlorides may be swept from the furnace by the sheath gas; they can also condense on the cooler ends of the furnace.* Low temperature volatilisation can partly be countered

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* For longitudinally mounted furnaces, the tube ends are cooler than the centre because they are in contact with the

by reducing the pyrolysis temperature to retain the analyte chloride. However, this creates further problems when the chloride matrix components and analyte are co-volatilised on atomisation. On atomisation, the furnace is heated directly by a high current, but the atmosphere inside the furnace is only heated indirectly through convection and radiation from the furnace wall. Because of this indirect heating, there is a temporal lag between the temperature of the furnace wall and the atmosphere inside the furnace. Therefore, when analyte chlorides are volatilised from the furnace wall, they enter a gas phase of a lower temperature. If the temperature is too low, the analyte chloride may be expelled from the furnace before it can be atomised. In some cases, where the analyte is volatilised in atomic form, it may react with chloride species (especially hydrogen chloride) in the cooler gas phase to form molecular species —thus reducing the atomic population and hence absorbance. This has a two-fold effect on analysis. Firstly, molecular chloride formation lowers the apparent atom concentration, decreasing sensitivity; and secondly, the molecular absorbance adds to the background that must be subtracted by the background correction system. Chlorides condensed in the furnace ends during drying and pyrolysis contribute to this, but with one additional problem. Because the furnace-end temperature lags behind that of the middle, species at the furnace ends are volatilised and atomised later than species in the middle. This change of atom supply rate, serves to broaden the analytical absorbance profile and can also decrease sensitivity. In extreme cases, double absorbance peaks, or sample carryover have been observed. Cumulatively, the extensive problems encountered with chloride interference are so severe that in some cases, such as seawater analysis, the sodium chloride content is too high to allow the direct determination of many metals unless remedial measures are taken.

Three different approaches are commonly used to combat chloride and other chemical interferences: the *stabilised temperature platform*, *chemical modification*, and *matrix removal* methods.

1.3.2.1 The Stabilised Temperature Platform

In L'vov's original graphite furnace atomiser,[7] the sample was atomised into a pre-heated (isothermal) furnace; a furnace design that suffered from fewer interference problems than are encountered with the Massman-type furnace.[19,20] This is largely because in an isothermal furnace, the sample and concomitant interferents are atomised into an atmosphere of sufficient temperature to effect complete dissociation. Several isothermal furnace designs have been proposed. Woodriff and Ramelow[21] introduced the sample into a preheated tube using a small graphite cup, while Manning et al.[20] dried the sample onto a tungsten wire which was then introduced to the preheated furnace. An alternative approach was taken by Chakrabarti et al,[22] who used rapid furnace heating (up to 100 K ms^{-1}) to reduce the lag time between heating the furnace tube, and the furnace atmosphere. Due to its simplicity, the most commonly adopted means of approximating isothermal furnace conditions is the *L'vov* or *stabilised temperature platform* (STP). First suggested by L'vov,[23] the stabilised temperature platform is a small piece of pyrolytic graphite which is installed

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water-cooled electrodes.

in the graphite furnace as shown in Figure 1.6. Graphite is a poor thermal conductor, and because the platform is in minimal contact with the furnace, it is heated indirectly by the furnace gases rather than by the furnace walls. Because of this indirect heating, the temperature of the platform lags behind that of the furnace gases and walls. Sample deposited on the platform is volatilised into a hotter (and approximately isothermal) atmosphere, thus minimising vapour-phase interferences.

Although isothermal furnace designs have greatly reduced the effects of many interferents, they still do not prevent the loss of volatile samples during pyrolysis. To seek a solution to this problem, analysts have turned to chemical modification.
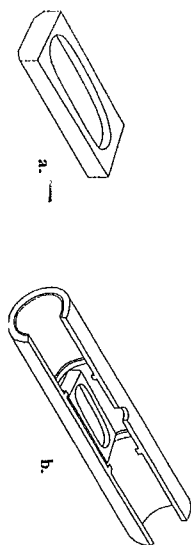

Figure 1.6 (a) The stabilised temperature platform, and (b) cutaway view of the platform installed in the furnace.

1.3.2.2 Principles of Chemical Modification

The objectives of chemical modification are to increase analytical sensitivity, and/or to reduce the effects of interferents. These are achieved by adding an excess of a reagent (modifier) which chemically alters the analyte, the sample matrix, or the furnace surface. There are two principal mechanisms by which chemical modification can improve the properties of an analyte.

Firstly, adding an excess of modifier ensures that the analyte is all present in the same chemical form and is atomised via the same mechanism. Usually, such a modifier includes an anion that forms a thermally stable compound with the analyte. A common example of this type of modification is the addition of nitric acid to samples prior to analysis. Unless high concentrations of other matrix components (e.g. chloride ion) are present, the modification ensures that the analyte is all present as a nitrate. This increases thermal stability for many volatile analytes, and promotes uniform atomisation characteristics.

Secondly, modification can be used to decrease analyte volatility; this "analyte stabilisation" has numerous beneficial effects on sensitivity and on interference reduction.

(i) Reduced analyte volatility prevents analyte losses and transport in the furnace during the pyrolysis stage.

(ii) When the analyte is thermally stable, higher pretreatment temperatures can be used. This permits more efficient interferent removal during the pyrolysis stage.

(iii) For a thermally stabilised analyte, atomisation is delayed until higher temperatures; at this point, furnace conditions are closer to isothermal. The increased temperature gives improved dissociation of volatilised species and hence reduces vapour phase interferences and improves sensitivity.

(iv) When modification increases analyte stability relative to that of interferents, there is a greater temporal separation between the analyte and background signals on atomisation. This permits more effective background correction and reduces the likelihood of interfering gas phase reactions between the analyte and other matrix components.

There a variety of mechanisms by which a modifier can thermally stabilise an analyte. The mode of action generally depends on the type of modifier. Tsalev et al.[24] have recently proposed classifying inorganic matrix modifiers into three main groups:

Group 1: Includes Mg, Ca, Sr, Sc, Y, La, Ba, Ce and Al. In the graphite furnace, up to temperatures of 1300-2000 °C, these modifiers are present as refractory oxides. At higher temperatures, they form salt-like carbides. These metals probably stabilise analytes by forming mixed oxides between the analyte and the modifier. Thus the analyte is occluded within the refractory bulk matrix of modifier.

Group 2: Includes Ti, Zr, Hf, V, Mn, W, Fe, Co, Nb and Cr. The oxides of these modifiers are transformed to metal-like carbides at lower temperatures than the first group of metals. Analyte stabilisation is probably effected by occlusion within refractory modifier oxides at low temperatures before the modifier begins to form carbides.

Group 3: "Metal" modifiers: include: Ni, Cu, Rh, Pd, Ag, Ir, Pt, Au, and Ru. Salts of these metals are reduced to elemental form at relatively low temperatures, generally below 1000 °C. These modifiers are thought to thermally stabilise analytes by forming solid solutions and/or analyte-modifier compounds that are entrapped within the bulk modifier.

A number of organic modifiers such as ascorbic acid, EDTA and Triton X-100 have also been used successfully. Organic modifiers work in different ways depending on their class. Strong complexing agents such as EDTA displace chloride from the analyte, thus preventing low temperature loss of volatile chlorides.[25] Modifiers such as ascorbic acid are believed to work by assisting analyte reduction (to metallic form). Thermal decomposition of the modifier during pyrolysis, forms carbon monoxide and active carbon which are dispersed with the analyte. Analyte reduction by the active carbon leads to enhanced atomisation kinetics and hence improved sensitivity.[26]

An alternative approach to analyte stabilisation is to promote the atomisation of volatile elements, before matrix vaporisation begins. This method allows temporal separation of the analyte and background signals. For example, Guevremont[27] used a citric acid modifier to directly determine cadmium in seawater. Modification was effected by mixing the seawater sample with 0.1% (w/w) citric acid solution. Upon analysis, sharp cadmium absorption peaks were obtained with maximum absorbances at 600 °C; the background absorbance did not become significant until temperatures above 900 °C. The authors used the same approach to determine zinc in seawater.[28] A citric acid concentration of 0.5% (w/w) produced zinc peaks with maxima at 650 °C; the background absorbance did not become large until temperatures above 1000 °C.

Other reported analyte modifications include decreasing the thermal stability of non-volatile and carbide-forming elements. For such elements, adding suitable modifiers increases sensitivity, and allows reduced atomisation temperatures and durations—resulting in increased furnace lifetimes. Nater et al. successfully applied this technique to aluminium determination.[29] Addition of a fluoride modifier promoted aluminium atomisation as fluoride at 1630 °C. The atomisation temperature (using the same experimental setup) of the more usual aluminium oxide was estimated at 1785 °C. A similar technique was used by Scott et al. to determine molybdenum.[30] A fluoride modifier decreased the molybdenum appearance temperature, and increased sensitivity by as much as 80%; interference from biological sample matrices was also reduced.

As an alternative to modifying the analyte properties, interferences can be reduced by altering sample matrix properties. The classical approach to matrix modification has been to convert interfering concomitants into volatile species that are more readily eliminated during the pyrolysis stage. An example of this, is the addition of ammonium modifiers to chloride-containing samples to promote ammonium chloride formation: this sublimes at a temperature of only 340 °C, compared to sodium chloride which boils at 1413 °C.[31]

Properties of Chemical Modifiers

In addition to its modifying properties, a useful chemical modifier must have several other attributes.

(i) The modifier must be available in a highly pure form so that it doesn't contribute trace amounts of analyte to the analysis.

(ii) The modifier must not contain an element that may be a future analyte. Some modifiers irreversibly contaminate the graphite parts of the atomiser and cannot be determined at a later stage as analytes. An example of such a modifier is nickel, which is also a routinely determined element.

(iii) The modifier should not contribute any background absorption of its own. For example, phosphate-containing modifiers which were popular in the early development of ETAAS, produce a UV spectrum that often requires Zeeman-effect background correction.[24]

(iv) Some modifiers such as lanthanum have been shown to corrode graphite.[32] The change in surface morphology degrades long-term stability, and shortens furnace life. Such modifiers are less than ideal.

(v) Modifiers should be non-toxic: reagents such as barium, chromium, manganese and thorium, which produce toxic or carcinogenic vapours are undesirable.

(vi) Some modifiers are prone to hydrolysis and are difficult to keep in solution. The ideal modifier is chemically stable.

In addition to the afore-mentioned properties, the ideal modifier would be applicable across a wide range of elements and sample matrices. Since the inception of ETAAS, scores of prospective modifiers have been suggested and trialed, however, most of these modifiers have fallen short in one

or more aspects of their performance.* The fact that so many possible modifiers exist, suggests in itself that selecting a chemical modifier for a particular analytical problem is a demanding task. To simplify modifier selection and to reduce the range of modifiers required, a popular goal has been to identify a chemical modifier that is effective across a wide range of applications.

Research over the past ten to fifteen years has determined that a "universal modifier" does indeed exist. Palladium, and combinations of palladium with other metals (or their salts) have been shown to thermally stabilise most volatile analytes (in a variety of matrixes) by hundreds of degrees, thus improving sensitivity and reducing interferences for many elements.[36] Although hailed as a universal, and therefore general purpose modifier, the performance of palladium is not necessarily inferior. For many elements, palladium is demonstrably superior to alternative, more specialised modifiers.[37] Thus, for many applications, palladium has become the modifier of choice.

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* A discussion of the many modifiers that have been proposed, their uses, properties, and their modes of action, is beyond the scope of this introduction. However, for further information the reader is directed to several excellent reviews on chemical modifiers. Modifiers in general have been reviewed by Carrick et al.[33] Ni and Shan,[34] and Tsalev et al.[24] Organic modifiers have been recently reviewed by Volynskii.[25] Tsalev has collated a bibliographic index of articles devoted to various aspects of chemical modifiers published between 1973 and 1989.[35]