SASKATCHEWAN ISOTOPE LABORATORY

Geological Sciences

Laboratory Practice Guide

SASKATCHEWAN ISOTOPE LABORATORY

Laboratory Practice Guide

Department of Geological Sciences
University of Saskatchewan

Compiled by: Bruce Eglington, Jock Harmer, Susan Haasbroek, Malherbe Auret, Mari Rademeyer, Kevin Ansdell, Bill Patterson, Chris Holmden

Table of Contents

Volume 1

General Procedures

1 Introduction

General philosophy for users of the isotope laboratory facilities.

Recommended procedures and various useful information have been compiled together into this manual so as to facilitate use of the isotope facilities by all users. The manual includes sections of relevance to staff who maintain the facilities, to users of the facilities and is also intended as a general reference to techniques used in this and other laboratories.

All procedures utilised in the SIL facility should adhere to safety procedures expected by the University. Deviations from these procedures are not acceptable.

The procedures documented should not, in any way, be regarded as final. Constructive, practical suggestions for improvements are welcome. As individuals develop new procedures or modify existing one it would be appreciated if these are documented and provided to the Laboratory Manager for incorporation in the Guide.

1.1 Analytical capabilities of the facility

1.1.1 Equipment

Micromillers for preparation of minute carbonate samples

MAT 253 GIRMS with Kiel sample introduction system

Delta-Plus GIRMS with TC/EA sample introduction system

MAT 261 TIMS

Triton TIMS

Neptune multicollector ICPMS

Ultraclean chemical laboratory

1.1.2 Preferred sample types

Silicate rocks and soils

Water, brines, etc

Carbonate rocks, minerals, compounds

Organic matter

1.2 Individuals involved in the operation of the facility

1.2.1 Management structure

The facility is governed by a Board of Directors and the Laboratory Manager. This Board defines policy for the Saskatchewan Isotope Laboratory which is then implemented by staff of the facility. Technical staff within the facility, or in support of the facility, each have primary areas of responsibility although cross-training is encouraged wherever practical.

1.2.2 Isotope facility and Geological Sciences

Staff involved in the running of the facility are:

Dr Bruce Eglington - Laboratory Manager. Extension 5732

Prof Chris Holmden – Director. Extension 5697.

Prof Bill Patterson – Director. Extension 5691.

Prof Kevin Ansdell – Director. Extension 5695.

Jim Rosen – Electronics technician. Extension 5711

Tim Prokopiuk– Stable isotope mass spectrometry technician. Extension 5712

Daphne Cordeiro – Chemistry technician. Extension 2243

Lloyd Litwin – Electronics technician. Extension 5709

1.2.3 Other university departments or sections

1.2.4Other organisations

A database, available on the SIL web site, provides details of organisations which supply items for the facility. This database may be accessed from web browsers at http://www.usask.ca/geology/isotope

2 General laboratory practice

1.1 Safety

A safe working environment is the most important component of any organisation or laboratory. It is the responsibility of each individual working in such a facility to ensure that his or her task can be completed safely and without causing injury to others. Safety procedures should not only be concerned with the immediate task at hand but also with all further hazards such as the safe disposal of waste products. It is furthermore, the responsibility of every individual to ensure that they inform their colleagues about any hazardous procedure they may be performing. Hazardous or dangerous situations, procedures, instruments or chemicals should be clearly marked. No task, experiment or procedure should be started unless it can be completed with safety.

Correct use and proper maintenance of equipment are important components of a safe environment, which can only be maintained with appropriate guidance and training of laboratory personnel. Training should always include guidance on proper cleaning procedures. Cleaning is vital in any isotope application where very small samples are handled and should be included in the planning of laboratory procedures. It is also the responsibility of all individuals using a facility to be familiar with emergency cleaning procedures relating to chemical spills.

One purpose of this manual is to provide recommendations on basic safety procedures in the isotope laboratory and associated facilities and to inform personnel of possible hazardous conditions. It is however still the responsibility of any individual using such facilities to ensure that he or she is familiar with appropriate safety procedures and to compile new safety procedures when necessitated by the implementation of new techniques, facilities or equipment. **If you are not sure, ask!!!**

Laboratory coats and gloves must be worn when chemicals are handled. It is essential that all new users of apparatus and equipment receive adequate training, with subsequent supervision available as appropriate. Regular assessment of hazards should be considered as a precaution against complacency. Adherence to known safe working practices will minimise the possibility of accidents. General tidiness and ensuring serviceability of all the apparatus and equipment are also vital.

2.1 Clothing

It is important to bear in mind that, although lab wear affords some protection from reagents to the wearer, its prime purpose is to protect the laboratory from ***you***!! Suitable lab wear must be used at all times. Thus, normal shoes must be left outside the mass spectrometer clean room or overshoes worn; and specialised clean suites and overshoes must be used in the clean laboratory.

Protective gloves and glasses **must** always be used when working with hydrofluoric acid and should be used with all acids.

2.2 Mass spectrometer laboratory – outer area

Normal shoes and clothing may be used in this area.

2.3 Mass spectrometer laboratory – inner area

Slip-on sandals or over shoes are to be worn. If using slip-on sandals, then normal shoes are to be left in the outer area.

2.4 Clean laboratory

Special, chemical-resistant lab suites and overshoes are to be worn. If 'low-level' work is to be carried out, then protective headgear should be put on.

2.5 Vacuum equipment

2.5.1 General

The use of vacuum is widespread within the isotope laboratory. Glass vacuum lines, mass spectrometers and dewar vessels all use vacuum. Vacuum apparatus made from metal may usually be considered low risk, while apparatus made from glass should be considered high risk due to the possibility of implosion. In some circumstances an explosion can occur in a system due to gas build-up. This may be eliminated by monitoring the pressure with appropriate pressure transducers. Appropriate eye and face protection must be worn when using any vacuum line and other apparatus liable to implosion.

2.5.2 Glass vacuum lines

The function of a line will frequently determine the major associated hazards. It is recommended that glass vacuum apparatus be screened but this may be restrictive to the operator if frequent access is required. To maximise safety, a compromise between full and no screening requires the careful selection and use of personal protection combined with appropriate screening, or other safety measures, deployed at those sections of the rig considered liable to cause greatest injury or damage in the event of failure. Large storage bulbs should be shielded or covered with an appropriate material to minimise the scattering of glass fragments should there be an implosion or explosion. Quartz glass is more brittle than soda or borosilicate glass and presents a particular hazard (very sharp) when fractured.

Leakage of air into a vacuum system that uses liquid nitrogen traps can be dangerous due to the possibility of liquification of air. If this is suspected (the presence inside the trap of a clear liquid with a bluish tinge), immediately inform an experienced person if you have not dealt with this problem before. Do not remove liquid nitrogen from around the traps.

Vacuum lines often have highly experimental designs. Electrical cabling, gauges, pumps, etc. are seldom mounted in neat cabinets, leaving exposed electrical connections which may be very dangerous to an inexperienced person. Although such equipment should be screened off it is the responsibility of the operator to avoid all loose wires and uncovered-screened electrical equipment to limit the possibility of electrical shock.

2.5.3Stresses and strains

Apparatus manufactured by the glassblower will normally be annealed to remove stress. Glass vacuum lines are likely to have areas under stress due to in-situ construction, which are liable to fracture under normal usage. The use of flexible tubing at appropriate positions, such as the connection between a rotary pump and a glass rig, will help minimise strains.

2.5.4Glass dewar vessels

The exteriors of glass dewar vessels should be adequately protected to contain debris following an implosion. Dewars containing a refrigerant should have secure bases and where appropriate each should have a lid to be fitted when not in use. Stirring the contents of a dewar is inadvisable, especially with a metal object, due to the possibility of scratching the surface and inducing cracks. If stirring is necessary, use a rod made of a material softer than glass (wood or plastic).

2.5.5Rotary pumps

All moving parts must be covered and manual rotation of a pump should never be attempted with the power on. Exhaust gases must not be allowed to accumulate in a room, especially when the pump is on gas ballast or pumping large volumes of gas. Fit appropriate filters or vent to the outside. On no account should the exhaust port be allowed to become blocked.

2.5.6Diffusion pumps

The heated areas of diffusion pumps should be screened to prevent accidental burns.

2.5.7 Turbo pumps

2.5.8Gauges

Many types of gauges are available to monitor vacuum or pressure. All require an electrical supply, while penning types require high voltages to operate. Appropriate precautions must be fully understood and exercised before any maintenance or repair work is undertaken.

2.5.9Spark tester

Do not operate a spark tester under damp or wet conditions or in an atmosphere which contain a high proportion of conductive dust particles. Do not operate a spark tester within 10 metres of sensitive electronic equipment. The spark tester is unlikely to cause a serious shock if the probe is accidentally touched although people with an incipient heart condition may be at risk. The reflex action from receiving a high frequency shock while working close to dangerous equipment may prove hazardous. Injury will occur when the spark is directed at sensitive parts of the body (such as the eyes). Do not place the probe near a conducting surface when it is switched on as arcing may occur through the side of the probe. The spark tester will generate ozone during

operation. In a confined space, it is possible for the ozone level to exceed the recommended safety limits and present health risk.

2.6 Mass-spectrometers

All mass spectrometer contain sections which operate at high voltage. Safety interlocks are provided on these machines to protect users. Do not over-ride these interlocks unless absolutely necessary and you know what you are doing. Machine repairs involving the high voltage sections of the mass spectrometers may only be performed by properly trained staff with the express knowledge of senior staff of the isotope facility.

2.7 Reagent preparation

Reagent cleaning, preparation and titration is to be carried out in the distillery sections of the chemical laboratory, and it is the responsibility of one staff member to maintain a supply of clean water, concentrated acids and selected reagents commonly used by most users. Preparation of specific concentrations of acid is ultimately the responsibility of the user, but may be arranged ***in advance*** with this person.

Reagents are labelled with "x" for each pass through a still, and "r" for each pass through ion-exchange resin. The analytical grade starting material is "GR", and 'suprapur' grade can be labelled "SP". It is important that all containers are clearly marked with the type, strength and "pedigree" of the reagent. A "Dymo" tape labeller is recommended, and a unit is available for this purpose. Each reagent type may then be conveniently colour-coded.

The following reagents are routinely produced:

Blue - H_2O

Red - HCl^{x} and HCl^{GR} at "constant boiling" strength (ca. 6.4M)

concentrated HCl^{x} (22%)

Green - HNO_3^{x} (concentrated, ca. 15M)

3M HNO_3^{x}

Yellow HBr^{R} (0.5M)

Black - HF^{x} (and HF^{x} by arrangement) (45%).

Water is initially purified by means of reverse osmosis which acts as the source to 18 Mohm Milli-Q devices in the laboratory. Care must be taken to not contaminate the dispensing spouts of these devices as this will affect all subsequent work in the laboratory.

Concentrated HCl is distilled in a teflon sub-boiler. The acid prepared in this way is then diluted as necessary.

Concentrated HNO_3 is sub-boiling distilled in teflon.

HBr (0.5M) is most easily cleaned on an anion-resin column. As HBr has a very high affinity for Pb (including atmospheric), this reagent should be cleaned in small batches in a controlled atmosphere in the laboratory. A large two-pass column is available for this purpose.

Concentrated HF is produced in a teflon sub-boiling still.

2.8 Laboratory ware

Where the budget permits, Teflon, either PTFE (white), FEP (translucent) or PFA (translucent) containers should be used and, unless explicitly stated otherwise, all sample dissolution containers should be of these materials. Elsewhere, polypropylene and polyethylene containers and disposable polypropylene beakers are used. Glass containers of any form, particularly those made of borosilicate, should be used as little as possible since borosilicate contains lead. Where no alternative to glass is easily available, quartz glass should be used in preference to borosilicate glass.

Concentrated HNO_3 can only be stored in Teflon, as it will discolour and etch polyethylene (PE) and polypropylene (PP). Concentrations of 5M and lower may be stored in PP or PE. Where possible, PP is a better storage material than PE. Measuring cylinders of "TPX" or “PMP” are recommended, as they have high chemical resistance (including HNO_3), are glass-clear, and have excellent liquid-release properties.

Temperature and chemical resistance of various plastics are shown below:

Type	HNO_3		HCl, HF		Max temp. (°C)
	Conc.	<5M	Conc.	<6M	
PP	N	G	G	G	120
PE	N	G	G	G	80
PTFE, FEP, PFA	G	G	G	G	200
PMP	N	G	G	G	120
TPX	G	G	G	G	175

G = good

N = not acceptable

2.9 Cleaning procedures

2.9.1 Introduction

Careful cleaning of laboratory equipment and work surfaces is essential. The successful determination of isotope ratios in small samples requires quantitative conversion of the sample to its analytical form without contamination that invariably results from dirty equipment. The accuracy of analyses is thus directly dependent on the care taken in cleaning the equipment. Leaving equipment and working surfaces dirty may cause analytical problems while failure to clear up spills of hazardous chemicals may put everybody working in the laboratory at risk. It is the responsibility of the individual to ensure that all equipment is cleaned and put away in the appropriate place on completion of their task. Leave time at the end of the working period for this purpose.

2.9.2Glassware.

The method of cleaning glassware depends on the type of contaminant and the type of glass. Vacuum grease may be removed by rubbing with a paper towel soaked in trichloroethylene or immersion in trichloroethylene until the grease has all dissolved. Rotary pump oil is difficult to remove with trichloroethylene alone. Use alternating application of trichloroethylene with soap and water. General laboratory dirt may be cleaned by immersion of the object in Teepol solution for 10 minutes, followed by rinsing with plenty of water. Teepol will not clean items coated in vacuum grease. Never put visibly wet items in an oven. Most of the water on glassware can be removed by wiping with paper or blowing with a hand drier. Never put greasy items in an oven. Only items which need to be kept hot until just prior to analysis should be stored in an oven. All other items should be removed and stored in the appropriate place when properly dry.

Quartz glass reaction tubes used in the tube furnace of a sulphur extraction line should be cleaned in a 30 % hydrofluoric acid solution for about one hour and then immersed in distilled water for another hour. The larger outer quartz glass tube should be cleaned by flushing it with concentrated nitric acid and then washing with Teepol solution and water. Periodic immersion in hydrofluoric acid may be necessary to remove burnt in contaminants. Always inspect glass tubes after cleaning for remaining contaminants or fractures. If contaminants are still visible after the first cleaning cycle then the procedure should be repeated. Discard cracked glassware immediately. The hydrofluoric acid cleaning procedure is one of the most dangerous exercises in the an isotope laboratory and should only be performed by trained personnel. The specific safety procedures applying to hydrofluoric acid should be strictly followed.

2.10 Sample tracking procedures

Volume 2

Safety

3 Safety in the Laboratory

3.1 Acids

3.1.1 HF

HF IS DANGEROUS

HF is an extremely dangerous and corrosive acid, forming fluorides in body tissues that are extremely difficult to displace. Furthermore, HF fumes, if inhaled, may cause irreparable lung damage. Disposable plastic gloves are provided and should be used whenever handling HF storage bottles or beakers containing HF. Before using this acid, read the available instructions on HF burns, and ensure that calcium gluconate ointment is available

3.1.1.1 Chemical properties

Hydrofluoric (HF) acid is a colourless fuming liquid (boiling point 67°C) which emits fumes similar to chlorine. HF acid has a variety of industrial uses such as glass etching, manufacture of fluorocarbons and electroplating.

3.1.1.2 Precautions in using hydrofluoric acid

Only personnel trained in the proper use of HF acid should be allowed to work with it. HF acid should only be used in approved facilities. Such facilities should include a fume cupboard with adequate extraction and running

water supply, HF-resistant beakers, measuring cylinders etc, explanatory notices on emergency procedures, an easily accessible tube of calcium gluconate gel and an eyewash bottle.

Extra care is needed when using HF solutions because of the consequences of inadvertent contact going unnoticed. People passing within 1 metre of the point of use of HF solutions must wear eye protection. People working with HF solutions must ware gloves and a laboratory coat (HF resistant) or plastic apron or cover garment. It is essential to have eye protection (full-face protection is recommended) as well as HF resistant footwear (open-topped shoes or sandals are not suitable).

3.1.1.3 Working practices

Personal protective equipment must be worn at all times. This should include full face protection, gloves and coat when using large quantities or protective glasses, gloves and coat for smaller quantities (a few ml). Gloves must be inspected for pin holes before being put on. PVC clothing should not be used. Contaminated clothing should be neutralised with sodium bicarbonate and washed before re-use, as should contaminated tools and equipment. After working with HF, hands must be washed immediately.

All personnel who use HF solutions must keep a supply of calcium gluconate gel and a copy of the emergency medical procedures for HF burns at home. Once the calcium gluconate gel has been opened it must be replaced.

Regular inspection, care and maintenance of equipment is essential. HF solutions must only be used in a fume cupboard, the front of which must be pulled down as low as practical. Trickles and splashes should be washed off immediately. Glassware must not be used as HF attacks glass. Any wet patches on work surfaces should be assumed to be HF acid and cleaned up immediately in the appropriate fashion. Contaminated porous materials e.g. wood, should be disposed of after contamination. All vessels should be washed out with water immediately after use (beware of splashes from high pressure supplies).

Procurement and storage of HF acid should be undertaken only by trained persons. Storage should be out of direct sunlight, away from heating pipes, containers kept tightly closed and the working area well ventilated. Containers should not be stacked higher than ground level. Acids supplied in polythene bottles and drums should be stored in the open, secured and access controlled. HF acid solutions should be transported with care, such as in a trolley or closed container. HF solutions must be disposed of with great care according to local arrangements.

3.1.1.4 Hazards from hydrofluoric acid

The hazards in the use of HF acid arise primarily from direct contact or vapour inhalation.

3.1.1.5 Skin burns

Contact can arise by means of spillage, liquid on outside of containers or vessels not properly washed. HF acid produces a burn with the following characteristics:

Intense throbbing pain, which may be immediate or occur after a latent period of up to 24 hours. In severe cases a tough white coagulum may be apparent over the burn, under which progressive destruction of tissue may continue (including bone) but lesser burns may not display any external sign. They are more serious than is first apparent because of deep penetration by the acid, the action of which is progressive, causing destruction of subcutaneous tissue over a period of several days.

3.1.1.6 Inhalation

Inhalation causes severe retrosternal pain and cough. Pulmonary oedema may occur, also after a latent period of up to 24 hours.

3.1.1.7 Eyes

The eye is particularly susceptible to burns, which again may occur after a latent period, leading to corneal opacities. Because of the penetrating characteristics of the acid, eye damage is likely to be more extensive than is first apparent.

3.1.1.8 Systemic

Systemic effects may occur after HF has been absorbed by any of the above routes as HF acid is corrosive to, and penetrates the skin and mucous membranes. Systemic effects are due to its corrosive action and due to calcium depletion following binding to fluoride. Subsequent hypocalaemia can result in tetany and cardiac arrest. The extent of systemic effects is related to the amount absorbed.

3.1.2Perchloric acid

Incidents and accidents involving the use of perchloric acid have been reported for more than a century. In 1947, 15 people were killed and 400 injured as a result of explosions caused by this acid.

3.1.2.1 Background

Pure, uncontaminated perchloric acid is extremely corrosive, but not explosive. At normal pressure, it may be safely heated to its boiling point with an open flame. However, once contaminated with an organic substance, or if it comes into contact with anything organic, even a wooden bench top, an explosion can occur. As the temperature of the operation increases, so does the hazard. Storage and handling should therefore be carefully controlled.

3.1.2.2 Handling

The proper and thorough use of personal protective equipment is imperative. Full-face shields should always be worn. When handling larger volumes, however, aprons, sleeves and gloves are also strongly recommended. The operator should be aware of the dangers involved when handling the acid or using it in a reaction. If the technician or laboratory worker is inexperienced, a senior person, familiar with the operation, should work alongside.

If it is suspected that a sample, to be reacted with perchloric acid, contains organic contaminants, it must first be treated with nitric acid. It is also good practice to run the fume hood for several minutes prior to and just after using perchloric acid. Running it prior to usage ensures that loose particles of dust are removed from inside the hood, minimising the chance of contamination. After the operation, running the hood at full force, ensures that the heavy acid fumes are completely removed.

3.1.2.3 Storage

Perchloric acid should be stored and used in a separate hood, preferably one constructed specifically for this purpose. Wooden or painted hoods should not be used. Fluorocarbon covered steel or other resistant materials are much better suited and hoods constructed of these materials are commercially available.

In laboratories, the acid should not be stored in greater than so-called Winchester-size quantities, and preferably in a strong glass or ceramic tray, large enough to hold that volume if the bottle should break. Discoloured, i.e. contaminated acid, should be disposed of at once.

A once a week inspection of all stock is considered good practice.

Mixtures of HF and perchloric acids are more effective for sample dissolution than HF alone or HF-HNO_3 mixtures, but beware:

- **Perchloric acid forms explosive mixtures with organic materials**
- **Perchloric is both difficult and dangerous to distil**
- **Specially designed fume cupboards must be used**

3.2 Other hazardous reagents

3.2.1 Bromine pentafluoride

3.2.2 Mercury

3.2.3 Tetrabromoethane

3.2.3.1 Chemical properties

Tetrabromoethane (TBE) is a very heavy yellowish liquid with chloroform-like odour. It is immiscible in water with a toxic level of 1 ppm (15 mg m^{-3})

3.2.3.2 Hazards from tetrabromoethane

Acute TBE poisoning may result in serious liver damage. TBE easily penetrates the skin, resulting in serious injury. When one can smell TBE the level of the dangerous concentration has been exceeded. The mutagenicity of TBE is readily demonstrable. TBE possesses the ability to react with the DNA of living cells and has the ability to devitalize cells.

3.3 MSDS data sheets

MSDS data sheets are available in the chemical laboratory and the mass spectrometry laboratory as well as in the main Geological Sciences office (room 114).

3.4 Chemical spills

All chemical spills should be treated in accordance with the procedures provided during the laboratory safety training courses provided by the University. Some reminders relevant to particular reagents are provided below.

3.4.1 Hazardous chemicals

3.4.1.1 Hydrofluoric acid

If there are fumes, evacuate the area and warn colleagues. If the spillage is not to be cleared up immediately, post warning signs and inform colleagues and superiors. Very small spills may be rinsed off with water. Larger spills may be absorbed on paper towels. Large spills should first be neutralised with $Ca(OH)_2$ and shovelled or mopped up.

3.4.1.2 Perchloric acid

Do not use absorbents such as sawdust, paper, cloth or other combustibles to soak up spills. Small spills should be soaked up with sand or other non-combustible absorbents, and the affected area washed with plenty of water. Spills can also be neutralised with a liberal amount of soda ash and mopped up cautiously with large amounts of water.

For large spillage, protective boots, apron, gloves and face shield should be worn. Spread sand or earth to contain spill by dyking, then call Health, Safety and Environment Services (x8493). If large amounts of the liquid have entered drains or sewers, the local authorities should be informed via HS&E.

It is also advisable to have a CO_2 fire extinguisher nearby when working with perchloric acid.

3.4.1.3 Other acids

Very small acid spills may be rinsed off with water. Larger spills may be absorbed on paper towels. Large spills should first be neutralised with Na_2CO_3 and shovelled or mopped up.

3.4.1.4 Tetrabromoethane

In the case of a larger spill instruct others to keep at a safe distance. Wear breathing apparatus and gloves. Apply dispersing agent and work to an emulsion with brush and water. The site of spillage should be washed thoroughly with soap and water.

3.4.1.5 Organic solvents

Will generally evaporate. Ensure adequate ventilation and avoid naked flames. If necessary evacuate lab.

3.4.1.6 Vacuum pump oil

Absorb on paper or other absorbent solid and shovel up.

3.5 Disposal of chemicals

3.5.1 Hazardous chemicals

3.5.1.1 Hydrofluoric acid

Very small quantities may be poured down the sink with a very large excess of water. Continue running sink for five minutes after all acid has been tipped away. Larger quantities must be poured into waste containers for disposal by contractors.

Tissue paper and plastic containers contaminated with HF should be placed in a marked bin for removal by contractors.

3.5.1.2 Other acids

Small quantities may be poured down the sink with a large excess of water. Continue running water for five minutes after all acid has been tipped away. Large quantities should be poured into waste containers for disposal by contractors.

3.5.1.3 Tetrabromoethane

Pour into waste containers for disposal by contractors. Tissue paper contaminated with tetrabromoethane should be placed in a marked bin for removal by contractors.

3.5.1.4 Vacuum pump oil

Pour into waste containers for disposal by contractors.

3.5.2 Other chemicals

3.5.2.1 Sodium polytungstate

Sodium polytungstate is extremely expensive and should be poured into a waste container for recycling.

3.5.2.2 LST

LST is extremely expensive and should be poured into a waste container for recycling.

3.6 Emergency management of HF burns

3.6.1 Introduction

Confusion exists concerning the immediate measures to be taken in cases of HF burns. The treatment recommended here is based on that published by the U&K Chemical Industries Association, Shell Chemicals and subsequently proven to be effective by practical experience.

Hydrofluoric acid (hydrogen fluoride, HF) exerts its harm mediated through two discrete actions. HF ionises and produces surface burns via the H ions - as with other strong acids. In addition, the F ions penetrate the tissues, destroying them until precipitated as magnesium and/or calcium fluoride, either by natural body, Mg and Ca compounds, or by those administered medically.

Pain is intense and immediate with concentrated HF, and intense but delayed with weaker solutions. The eventual systematic damage is, however, the same.

3.6.2 Rationale of first-aid

Until recently, neutralisation was the preferred treatment. However, precipitation of the F ions is the primary objective, and leads to immediate relief of pain and prevents further tissue destruction. In the case of inhalation of HF vapours, supportive treatment is given and attempts to precipitate the F ions should then be made systematically.

In eye burns, augmenting natural tear flow is preferable.

In all cases, calcium gluconate is the most effective fluorine precipitation measure.

3.6.3 First-aid measures

3.6.3.1 All cases

- Stop further contamination:
- Remove from environment.
- Remove contaminated clothing.
- Call a colleague.

3.6.3.2 Skin exposure

- Wash area liberally with copious amounts of tap water fort ***10 SECONDS ONLY***. (See note (i) below.)
- Let the injured party massage the special ointment (Ca-gluconate gel) into the contaminated area himself. (See note (ii) below.)

- Phone the university emergency/security services (x5555), reporting the burn and ask them to warn the hospital that a patient is to be brought in. Please note the concentration of the HF. (See note (iii) below.)

3.6.3.3 Inhalation exposure

- Phone the university emergency/security services (x5555), reporting the problem and ask them to warn the hospital that a patient is to be brought in. Please note the concentration of the HF. (See note (iii) below.).

3.6.3.4 Eye exposure

- Wash both eyes with copious amounts of tap water for 10 seconds.
- Instil 10 drops of the special eye drops in ***BOTH*** eyes.
- Phone the university emergency/security services (x5555), reporting the burn and ask them to warn the hospital that a patient is to be brought in. Please note the concentration of the HF. (See note (iii) below.).

NOTES

i. Other acid burns are usually irrigated for 10 minutes or more.

ii. Due to the intense pain, it is easier if the victim himself applies the ointment.

iii. The hospital must be warned ***BEFORE*** the patient arrives, as time is of the essence.

iv. ***NEVER*** leave an injured person alone. In more severe burns, they can go into shock and become disorientated. This delays proper treatment.

3.6.4First-aid boxes

First-aid boxes will contain the following in addition to the standard equipment:

· Eye wash bottle.

· Special ointment (Ca-gluconate) 2 kg.

NOTE that the preparations are sterile, and should not be tampered with. It is the responsibility of the appointed Safety Officer to keep the box up to date.

3.6.5Subsequent management of HF burns

It should be noted that reactions to contamination by dilute HF (<20%) may be delayed, and it is advisable for those at risk to keep a tube of the gel at home for initial treatment. If a delayed action burn occurs, the casualty should report to the designated hospital (Royal University Hospital - Casualty Dept, Tel. No. 655-1362).

Delayed pulmonary edema may develop many hours after serious burns or inhalation if HF fumes are inhaled. Hospital observation is desirable for at least 48 hours.

Relief of pain indicates success of treatment.

3.6.5.1 Skin

If the burn fails to respond to the calcium gluconate gel within 30 minutes an injection (into and under the burn) of 10% sterile calcium gluconate should be considered. Excision of necrotic coagulum should be considered as this is a barrier to the gel. If the burn is extensive, calcium and / or magnesium may have to be replaced (see below). In subungual burns, excision of the nail is advised. If pain recurs in the skin after treatment, treatment should be repeated.

3.6.5.2 Eyes

Continue irrigation and treat symptomatically (specialist ophthalmological opinion may be necessary).

3.6.5.3 Inhalation

Expect onset of pulmonary oedema and ensure all facilities are available for treatment. General anaesthesia should be considered with care.

3.6.5.4 Systemic

Hydrofluoric acid can be absorbed through the skin, respiratory tract, eyes and other mucous membranes and can produce systemic effects because of its corrosive action and because of calcium depletion due to fluoride binding. The subsequent hypocalcaemia can result in neuromuscular problems such as tetany and cardiac arrest. The extent of these complications is directly related to the amount of fluoride absorbed. In cases of extensive skin burns (larger than the palm of the hand) and in all cases of inhalation, estimation of calcium levels and administration of calcium by intravenous infusion should be considered. The calcium salt of choice is 10% calcium gluconate, which should be given slowly, avoiding extravasation. Serum calcium should be measured frequently, i.e. once every half an hour in severe cases.

3.7 Standard treatment for chemical accidents

3.7.1Inhalation

Remove casualty to safe area. Loosen clothing. If the casualty is unconscious place in a face-down position and watch to see if breathing stops. If breathing has stopped apply artificial respiration by the mouth-to-mouth method. If the emergency warrants it, call for emergency support and provide information on the gas responsible. Administer oxygen if available and if the casualty's condition is serious.

3.7.2Affected eyes

Flood the eye(s) thoroughly with large quantities of gentle running water either from a tap or an eyewash-bottle for at least 10 minutes. Ensure the water bathes the eyeball by gently prising open the eyelids and keeping them apart until the treatment is completed. All eye injuries from chemicals require medical advice. While giving treatment arrange transport to hospital and supply information to accompany the casualty on the chemical responsible with brief details on the treatment already given.

3.7.3Skin contact

Flood the splashed surface thoroughly with large quantities of running water and continue for at least 10 minutes. Removal of agents insoluble in water will be facilitated by cleaning the contaminated skin area with soap. Remove all contaminated clothing, taking care not to contaminate yourself in the process. If the situation warrants it, arrange for transport to hospital or refer for medical advice to the nearest doctor. Provide information on the chemical responsible to accompany the casualty with brief details of the first aid treatment given.

3.7.4Ingestion of chemicals

If the chemical has been confined to the mouth, give large quantities of water as a mouth wash. Ensure the mouth wash is not swallowed. If the chemical has been swallowed give about 250 ml of water to dilute it in the stomach. Do not induce vomiting as a first aid procedure. Arrange for transport to hospital. Provide information to accompany the casualty on the chemical swallowed with brief details of the treatment given and if possible an estimate of the quantity and concentration consumed and the time elapsed since the emergency occurred.

Volume 3

Clean Laboratory

4 Reagent preparation

4.1 Water

Water for the isotope clean laboratory is produced in a staged process. After initial filtering of the general supply, the water receives its first clean-up by means of a Millipore RX reverse osmosis facility. The reservoir tank from this instrument then acts as the feed to several Milli-Q 18 Mohm devices which provide ultraclean water for all subsequent laboratory activities. Flushing the reverse osmosis cartridge helps to prevent a build-up of debris on the membrane surface.

4.1.1 Operation of the Millipore RX

1. Make sure that the first two-way tap on the outlet pipe is positioned so that the water will run back to the sink.

2. Turn on the water supply.

3. Open the concentrate outlet valve for approximately 30-60 seconds, to flush the reverse osmosis cartridge.

4. Close concentrate outlet valve until pressure regulator gauge registers 60 psi. Flow should not be cut off completely.

5. The initial flow from the outlet will be of poor quality, and this should be discarded. Run the Milli RX for approximately half an hour, or until the conductivity meter registers 12 mega-ohms, before directing the water to either one of the storage containers. This is done by adjusting the first and second two-way taps on the outlet pipe.

6. When finished collecting H_2O, open the concentrate outlet valve for approximately 30-60 seconds, to flush the reverse osmosis cartridge. Close the valve and switch off the water supply.

4.1.2 Operation of the Milli-Q water systems

1.

4.2 HCl

HCl^{x} is produced by running a teflon sub-boiling still.

Operation of the HCl sub-boiling still

1. Any HCl^{x} in the collection bottle is placed in the storage containers provided for concentrated HCl^{x}.

2. If necessary, empty the HCl^{GR} and HCl^{x} overflow bottles from the first stills. The HCl^{GR} overflow is poured into the waste HCl container, and the HCl^{x} overflow is poured back into the HCl^{GR} storage container. These overflow bottles should be emptied *before* commencing distillation as a lot of distillation time is wasted if the stills have to be switched off, cooled and the overflow bottles emptied halfway through the day.

3. Fill the reservoir from a HCl^{GR} container.

4. Switch on the cooling water.

5. Switch on the heating element and timer.

6. The timer may be used to run the still after hours, provided that one is sure that run conditions are correctly set.

4.3 HF

HF is distilled in Teflon stills. HF^{GR} is distilled to produce HF^{x}. *HF IS DANGEROUS*. Gloves must be worn when changing the HF still, and this should always be done with two people present. The HF should be handled in a fume cupboard at all times.

4.3.1 Operation of the HF still

1. Switch off the heating element and allow still to cool completely.

2. The HF^{GR} bottle is filled with HF^{GR}. This is supplied in 500 ml bottles. The empty bottles can be kept for "HF waste". Periodically, the HF^{GR} and HF^{x} bottles should be emptied into the HF waste bottle, in order to remove the impurities which have built up in the remaining undistilled HF with time.

3. The HF^{x} is poured into the HF^{x} storage container, depending on requirement.

4.4 HNO_3

HNO_3^{GR} is sub-boiling distilled in a Teflon sub-boiling still.

4.4.1 Operation of the HNO_3 still

1. The still is operated in the same way as the HCl still. Periodically, it should be emptied in order to reduce the build-up of impurities in the undistilled HNO_3.

4.5 2.5M and 6M HCl

There are polypropylene measuring cylinders for making up the above acids. Acids should be made by alternatively adding the water and acid in roughly the correct proportions to the storage container. This helps to speed up the mixing and equilibration process considerably.

4.5.1 Making 2.5M HCl

The 2.5M HCl^x is made using 6M HCl^x and H_2O. There are two 25 l containers for 2.5M HCl^x. This allows for a batch of 2.5M HCl^x to be made prior to requirement. The acid should be made and left to stand for a few days, and then titrated. If necessary, fill the 2 l measuring cylinder with acid from the tap and pour this back into the container. This can be done several times in order to aid mixing.

4.5.2 Making 6M HCl

The 6M HCl^{GR} is made using H_2O and concentrated HCl^{GR}. The latter has a molarity of approximately 10, and is obtained in 2 l bottles.

After making the 6M HCl^{GR}, it should be left to stand for a few days to equilibrate and then be titrated. This acid should be made to 6.5M ("constant boiling" strength) as closely as possible.

The 6M HCl^x is made using H_2O and concentrated HCl^x. The latter has a molarity of approximately 10.

After making the 6M HCl^x, it should be left to stand for a few days to equilibrate and then be titrated. This acid should be made to 6M as closely as possible.

4.6 HBr

As HBr has a very high affinity for Pb (including atmospheric), it is preferable to clean it in small batches in a controlled atmosphere in the Pb laboratory. The small amount of HBr^{rr} required by the Pb chemistry, allows small quantities of HBr^{GR} to be prepared and cleaned just prior to use. This should be done when commencing Pb chemistry on a batch of samples.

4.6.1 Making HBr

1. Two litres of 0.5M HBr^{GR} are made up in the 2 l polypropylene bottle provided. This need not be done accurately. The required amounts of HBr^{GR} and H_2O are marked on the bottle. Shake the bottle to mix thoroughly, and allow to stand for a day.

2. HBr is cleaned on an anion exchange column. A quartz-glass column containing approximately 50 g of AG2x8 anion exchange resin is available for cleaning the HBr. The HBr^{GR} is passed through the column once to produce HBr^{r} and this is then passed through the column again to produce HBr^{rr}.

3. Prepare the resin by passing through approximately 50 ml of 6M HCl^{x}, followed by approximately 50 ml of H_2O. The 50 ml volume is marked on the column. Put through approximately 1 l of 0.5M HBr^{GR}, and discard the first 100 ml. Collect the rest into the 1 l polypropylene bottle provided for 0.5M HBr^{GR}. Repeat the whole procedure to produce HBr^{rr}. The HBr^{rr} is collected into a 1 l Teflon bottle.

Try not to leave the HBr containers standing out on the shelf for any length of time, as light tends to facilitate the dissociation of bromine from the HBr.

4.7 H_3BO_3

H 1.00707 }

B 10.811 } atomic weight = 61.833

O 15.9994 }

Require 5 000 μg/ml = 5 mg/l B

B = 0.17484 of H_3BO_3

61.833 g H_3BO_3 contains 5 g B

⇒ 28.9 g H_3BO_3 contains 5 g B

⇒ 28.6 mg H_3BO_3 contains 5 mg B

Actual preparation was:

0.62 g H_3BO_3 in 501.45 g 3.0M HNO_3

Blanks for this solution were (including cation column chemistry):

Sr 36 pg/ml

Nd

4.8 Acetic acid

Given 100% acetic acid, to prepare 1 l 5M CH_3COOH requires 187.5 ml 100% CH_3COOH.

4.9 Preparation of silica gel

4.9.1 Method used by Urs Schärer

1. Blend $SiCl_4$ with ultra-clean water to form a gel suspension.

2. $SiCl_4$ obtained from Morton Thiokol Inc., 152 Andover Street, Danvers, Massachusetts, MA 01923. ALFA Chemicals catalogue number 88002. Another number listed was 10026-04-7. Ultrapure, 99%, sold in 250 g batch for $12.50.

3. Gives optimum performance at ~1400°C (routinely 0.9% per amu).

4.9.2 Method documented by Mike Cheatham

4.9.3 Method suggested by Khal Spencer

4.9.4 Method used by Brian Gulson

4.9.5 Method published by Gerstenberger and Haase

4.9.6 Method used by Andy Millwood

4.9.7 Method suggested by VG

The gel loaded onto the filament must be extremely fine.

Grind approximately 1 g of silica gel (60 HR extra pure Merck) in an agate mortar for 2 to 3 hours.

Introduce the powder into 15 ml of pure water and shake for a few minutes at 2-hourly intervals during the first day.

Allow the suspension to settle for 3 days. Decant the liquid and use as silica.

4.9.8Sodium metasilicate method

Dissolve 30 g of sodium metasilicate (natron) [$Na_2SiO_3 \times 9H_2O$] in 200 ml nitric acid (1+19). Evaporate close to dryness (at ~160°C), repeat the procedure, but evaporate to dryness. Add 200 ml nitric acid (1+99) to the residue and boil for 10 minutes. Filter the hot solution through medium porosity filter paper (Whatman 40). Wash the residue back into a bottle with H_2O^S (200 ml). Boil for 10 minutes and allow to cool for ½ hour. Decant the water and repeat 3 to 4 times. Dilute the residue with 10 times its own volume with H_2O^S and transfer to Teflon (du Pont) bottle. Shake the solution thoroughly 2 or 3 times a day for 3 days. After a 3-hour settling time, decant the upper liquid and transfer it to another du Pont bottle. This colloidal suspension is the silica gel to be used.

An alternative method has been described by using a quantity of a commercial silica gel powder used for thin layer chromatography (silica gel, 60 HR, extra pure, E Merck, Darmstadt, obtained from Brinkmann Instruments Inc, Westburg NY).

Approximately 1 g of this powder was ground in a new agate mortar for 2 to 3 hours to produce an extremely fine particle size. This material was then mixed with 15 ml of pure water and shaken thoroughly for a few minutes at 2-hour intervals during the first day. The solution was then allowed to settle for 3 days, after which the supernatant was carefully decanted and used as "silica gel".

The estimated particle size in either preparation is less than 0.4 μ. It is believed that silica gel particles of this size or smaller are required for successful use in mass spectrometry application.

4.10 H_3PO_4

4.11 Ag_3PO_4

This is from a poster presented at AGU, 2004 and is the procedure used at the Carnegie Institute.

1. Need 0.3 to 1 mg of $CaPO_4$ in a small centrifuge tube.
2. Add 300 μl of NaOCl (bleach), leave and vortex for 12hrs at room temperature.
3. Add 100 μl of 2M HNO_3 and leave for 20hrs at room temperature.
4. Add 33 μl of HF, and then immediately add 500μl of silver amine solution and 100μl of 1.25N NH_4NO_3. Then add 1 drop of 1:1 NH_4OH and Millipore.
5. Keep samples uncovered for 12 hours @ 50°C.
6. Wash crystals and separate white(?) crystals of CaF_2 from yellow crystals of Ag_3PO_4. Let crystals dry at 50°C in a N_2 atmosphere.

Comments: I am not sure how the CaF_2 and Ag_3PO_4 crystals are separated from each other. Maybe the CaF2 sinks to the bottom of the tube whilst the Ag_3PO_4 floats on the top. All of the HF is probably used

up (I haven't looked at the detailed stochiometry, but enough HF is probably added to take out the Ca. Try it out. It looks easy. The bleach oxidizes organics, and drying under N2 makes sure any excess silver or silver salts do not change colour, yielding nice yellow crystals all of the time.

5 Useful additional information relevant to reagent preparation

5.1 Constant boiling points of acids

Acid	Conc. (%)	Conc. (M)	T (°C)
HBr	47		126
HCl	20.24		110
HF	35.35		120
HNO_3	68		120.5

5.2 Calculating the molarity of mixtures in acids

Required molarity x required amount = $molarity_1$ x $amount_1$ + $molarity_2$ x $amount_2$.

5.3 Titration

Acids are titrated using either 1M or 0.1M NaOH titrasol and methyl red indicator. 1 ml of acid is normally titrated. Titrations are done several times and an average taken. After titrating, make sure that the burette is rinsed well with H_2O and the taps removed, as these tend to stick if left in. The titrasol is stored in a cupboard, and should be tightly sealed.

6 Preparation of ion exchange resins

6.1 Cation resins

Clean the resin in 5M HCl^x with 1% HF^x in a plastic container in an ultrasonic for ~2 days. Container should be shaken regularly and the supernatant liquid decanted and replaced with new liquid as often as seems necessary to achieve a clean supernate. The solution initially turns orange because of the suspension of fines in the supernatant liquid. Once clean enough, dry at ~95^oC overnight until all the acid has evaporated. Break up resin with a plastic spatula. Place resin in a squirt bottle and form a slurry with the appropriate acid ready to pack columns. Squirt resin into several measuring cylinders and allow to settle. Top up as necessary until all cylinders contain the required volume of resin.

AG50Wx12 200-400 mesh

Smaller columns. Cleaned and dried. 2.5 $\pm$ 0.0005 g aliquots weighed out.

Larger columns. Cleaned and dried. 5.0 $\pm$ 0.0005 g aliquots weighed out.

Subsequently, columns were prepared by selecting 5ml of resin in 6M HCl in measuring cylinders and then transferring all of the resin to the columns

6.2 Anion resins

Clean the resin in 5M HCl^x with 1% HF^x in a plastic container in an ultrasonic for ~2 days. Container should be shaken regularly and the supernatant liquid decanted and replaced with new liquid as often as seems necessary to achieve a clean supernate. The solution initially turns orange because of the suspension of fines in the supernatant liquid. Once clean enough, dry at ~95^oC overnight until all the acid has evaporated. Break up resin with a plastic spatula. Place resin in a squirt bottle and form a slurry with the appropriate acid ready to pack columns. Squirt resin into several measuring cylinders and allow to settle. Top up as necessary until all cylinders contain the required volume of resin.

This procedure is the same as for cation resin.

6.3 Kel-F resin

Teflon powder is combined with HDEHP (di-(2-ethylhexyl) phosphoric acid from Sigma) in the weight ratio 10 : 1 (powder : HDEHP) in an acetone slurry in a squirt bottle. The slurry is then dried at or near room temperature and can be stirred by a Teflon-coated magnetic stirrer until it becomes too thick. The dried powder is then slurried in H_2O and loaded into the columns as necessary. Each column is capped by a small amount of AG1x8 (200-400#) resin to stop the teflon powder from floating when reagents are added.

Columns used at the CSIR, South Africa and the Council for Geoscience, South Africa are: 10 cm of Kel-F in 6 mm ID columns, topped with 0.5 cm of Dowex AG1x8 (200-400#) anion resin.

The Max-Planck Institute in Mainz has batch number D-1509 lot 109C-0242 and used the following quantities:

40.02 g Teflon

4.06 g HDEHP

40.5 g acetone

The first batch made at CSIR, South Africa was:

18.6 g Teflon

1.86g HDEHP

186.0 g acetone

which took a long time to dry

The batch made in March 1991 at CSIR, South Africa was:

24.77 g Teflon

4.30 g HDEHP

117.0 g acetone

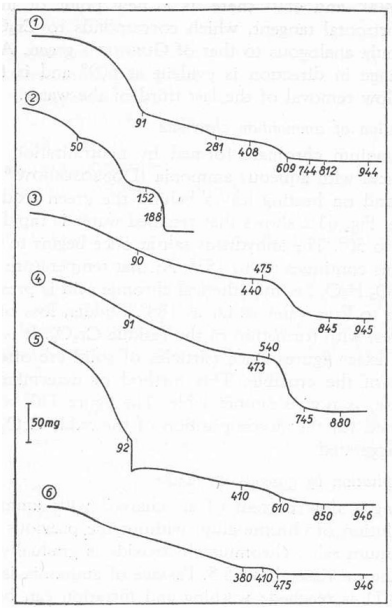
which was able to separate Sm from Nd in 0.4 M HCl with out changing acid strength between the elements.

6.4 LN resin

7 Thermogravimetry of compounds used to prepare gravimetric standards

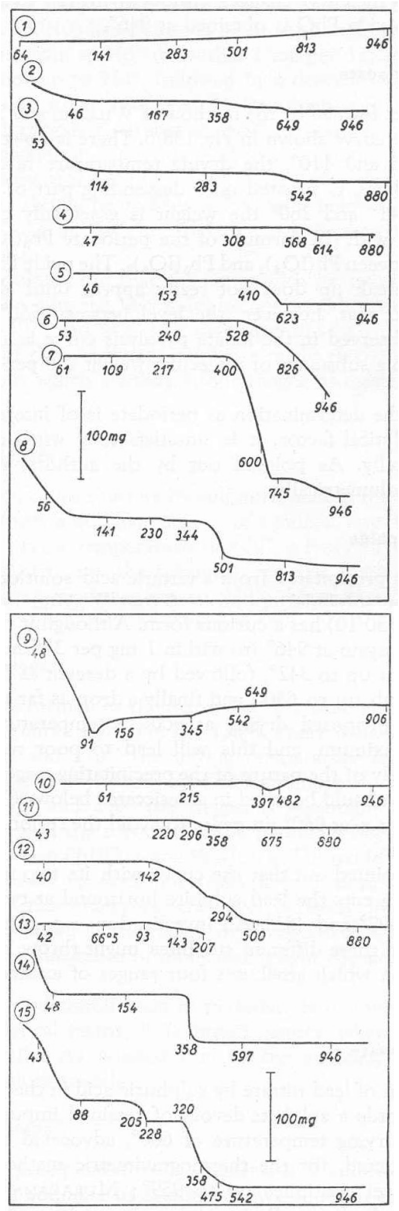
All pyrolysis curves in this section are from Duval (1953).

7.1 Chromium



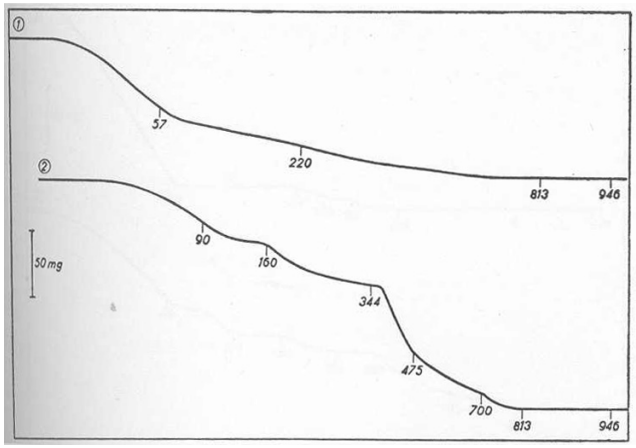
Pyrolysis curves of chromium hydroxide precipitated by: 1. aqueous ammonia 2. ammonium chromate. 3. gaseous ammonia. 4.aniline. 5. hydroxylamine. 6. thiosemicarbazide

7.2 Lead



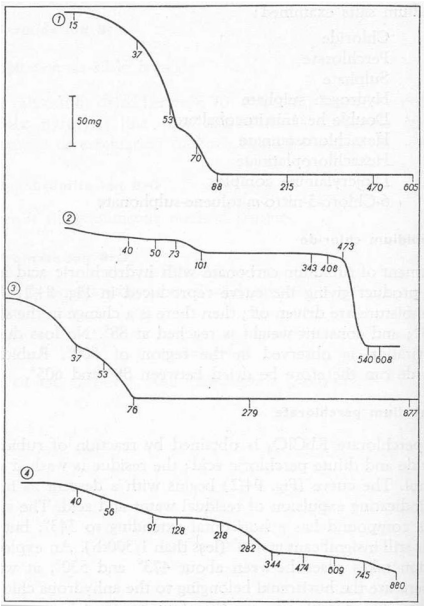
Pyrolysis curves of lead derivatives: 1. PbO from the metal 2. PbO from the oxide PbO_2. 3. PbO from the oxide $Pb_5O_7.3H_2O$. 4.PbO from the oxide Pb_3O_4. 5. PbO from the hydroxide. 6. chlodride. 7. iodate. 8. periodate. 9. sulphide. 10. sulphite. 11. hydrogen phosphate. 12. carbonate. 13. basic thiocyanate. 14. oxalate. 15. phthalate.

7.3 Neodymium



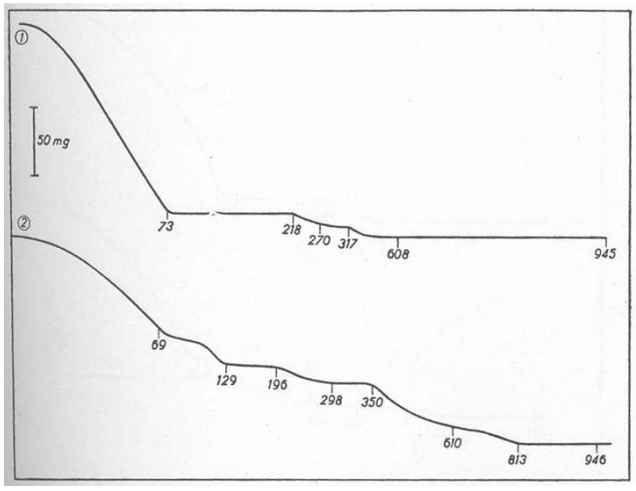
Pyrolysis curves of neodymium derivatives: 1. hydroxide 2. oxalate

7.4 Rubidium



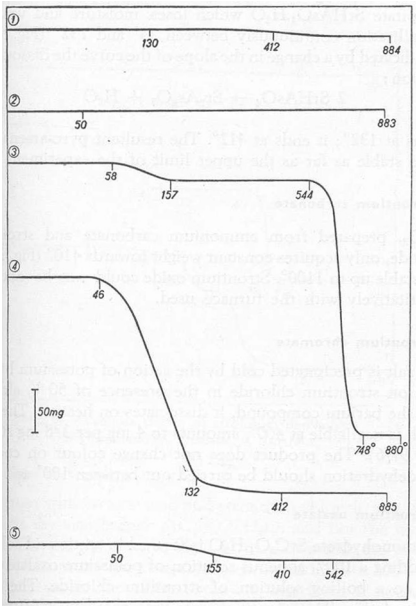
Pyrolysis curves of rubidium derivatives: 1. chloride 2. perchlorate. 3. sulphate. 4.hydrogen sulphate

7.5 Samarium



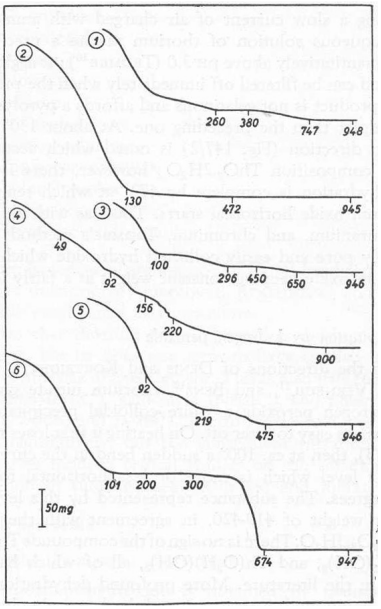
Pyrolysis curves of samarium derivatives: 1. hydroxide 2. oxalate

7.6 Strontium



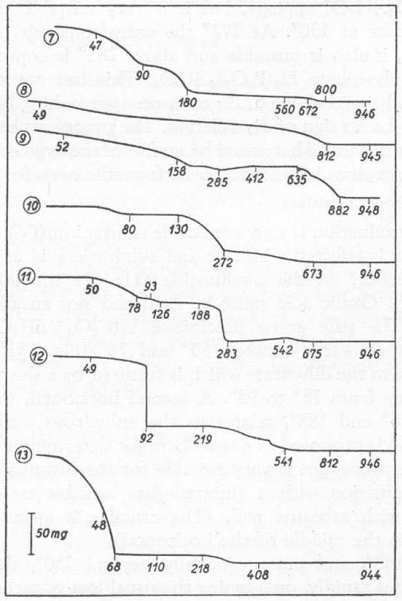
Pyrolysis curves of strontium derivatives: 1. sulphate 2. fluoride. 3. iodate. 4. arsenate. 5. carbonate

7.7 Thorium

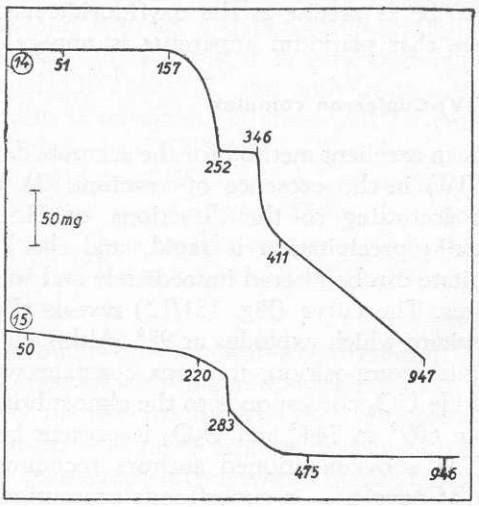


Pyrolysis curves of thorium derivatives: 1. hydroxide via aqueous ammonia 2. hydroxide via gaseous ammonia. 3. hydroxide via hydrogen peroxide. 4. hydroxide via hexamine. 5. hydroxide via tannin. 6. iodate. 7. selenite. 8. thiosulphate. 9. pyrophosphate. 10. oxalate. 11. fumarate. 12. sebacate.

7.8 Uranium



Pyrolysis curves of ammonium pyro-uranate precipitated by: 1. aqueous ammonia 2. gaseous ammonia. 3. pyridine. 4. ammonium benzoate. 5. hexamine. 6. tannin.



Pyrolysis curves of uranium derivatives: 7. uranium (VI) “peroxide”. 8. uranium (IV) oxyfluoride. 9. uranium (VI) oxysulphide. 10. uranium (VI) hydrogen phosphate. 11. uranium (IV) oxalate. 12. uranium (IV)-cupferron complex. 13. beta-isatoxime complex.

8 Cleaning of laboratory ware

8.1 Cleaning micro-centrifuge tubes, pipette tips and planchettes

Micro-centrifuge tubes are all stored in clean plastic sample bags. Two 2 l beakers with flat rims and watch glass covers, marked 6M HCl^{x} and H2O respectively, are available for cleaning micro-centrifuge tubes and they are to be used only for this purpose.

Where necessary, bulk-packed pipette tips may be cleaned using the same procedure. In general, though, pipette tips are purchased in precleaned, sealed racks. It is not necessary to clean these pipette tips before use.

PIPETTE TIPS USED ARE THROWN AWAY AFTER USE.

8.1.1.1 Cleaning micro-centrifuge tubes

There are two sizes of centrifuge tubes with caps: 1.9 ml and 1.5 ml. As they are made of polypropylene, 6M HCl^{x} is used for cleaning, instead of nitric acid, which discolours and etches polypropylene.

Half fill the HCl^{x} beaker with centrifuge tubes and add 6M HCl^{x}. Using Teflon tongs, push as many centrifuge tubes under the acid as possible, thereby allowing the acid to fill the tubes. Place the watch glass cover on top. This beaker may then be placed in an ultrasonic bath for a couple of hours. It must then be placed on a hotplate. The acid should be heated to a temperature of 60-80oC, and then left for a minimum of 48 hours. As the centrifuge tubes tend to float on top of the acid, it is advisable to periodically push them under the acid with Teflon tongs during this period. After 48 hours, each centrifuge tube is removed with a pair of Teflon tongs, taking care to shake off as much of the acid as possible, and is placed in H2O in the beaker provided. The H2O is then heated to 60-80oC and left for a further 24 hours, after which the centrifuge tubes should be individually rinsed with H2O using a squirt bottle and then transferred to the relevant storage container and stored under water. Before storing a new batch of clean centrifuge tubes, the old H2O should be replaced with fresh.

8.1.1.2 Cleaning planchettes

Samples which are not going to be run on the mass spectrometer immediately, may be transferred to planchettes and dried down. The planchettes are stored in 10 ml glass beakers, covered with cling-wrap.

Used planchettes should be removed from the glass beakers and wiped clean with roller towel and acetone. The sample label should be cleaned from the beaker using acetone. The planchettes and glass beakers are then placed in the respective plastic storage containers provided for used planchettes and glass beakers.

When a fair number of planchettes have been collected ready for cleaning, they, together with the glass beakers, are taken across to the distillery section of the laboratory. The planchettes are placed in concentrated $HNO3^{GR}$ in the 1 l beaker provided for cleaning planchettes. They are then placed on a hotplate in a fume cupboard and boiled for at least 1 hour. The boiling HNO3 is then poured off and they are rinsed twice in H2O.

They are then boiled in H2O for another hour, after which they are rinsed with fresh H_2O, and placed in a plastic container on roller towel or eggcrate and allowed to dry.

Meanwhile, the glass beakers are placed in Decon in the ultrasonic for an hour. They are then removed from the Decon, thoroughly rinsed under the tap to remove all traces of Decon, and placed in H_2O. Two beakers are provided for H_2O rinses. The beakers are rinsed twice in H_2O and placed on the drying rack to dry.

When both the planchettes and glass beakers are dry, the planchettes are transferred to the 10 ml beakers. One must wear plastic gloves when doing this. Take care not to touch the inside of the planchette. The beakers are then covered with cling-wrap and put into the plastic container provided for storing clean planchettes.

8.1.1.3 Cleaning Teflon ware

8.1.1.4 Cleaning Teflon beakers

Beakers should be rinsed with 6M HCl^x and H_2O to remove any traces of previous sample material. Persistent stains may require wiping with a paper towel soaked in acetone, followed by careful rinsing. Care must be taken not to touch the inside of the beaker with fingers. Add ~5 ml 6M HCl^x and leave the beaker on the hotplate for 1 hour. Discard the acid and rinse properly with H_2O. Beakers are then immersed in hot (ca. 60-80^oC) concentrated $HNO3^{GR}$ for 24 hours, rinsed thoroughly in H_2O, then soaked in hot H_2O for a further 24 hours. After removal, the beakers (and lids) are rinsed with fresh H_2O, shaken to remove excess water, then left to dry on eggcrating in a sealed plastic container. Beakers and lids should be placed with open ends down to allow any water to drain off. Proper drying is important and the beakers should be left to dry for at least 12 hours.

NOTE: This procedure is efficient for cleaning beakers having smooth internal surfaces, such as moulded FEP Teflon beakers and "Savillex" vials. If it is suspected that the beakers are less perfectly made, or where samples of extreme compositions have been processed (e.g. micas, pegmatite minerals), it is safer to boil the beakers in concentrated $HNO3^{GR}$ prior to soaking in clean HNO_3-H_2O.

8.1.1.5 Cleaning Krogh-type bombs

Between samples, fill the base and cap with 6M HCl^x and heat on a warmer for about an hour. Discard acid and rinse with H_2O. Add 1-2 m HF^x and 1-2 drops HNO_3^x, seal, put on shrink sleeves and place in steel bomb in the oven at 220^oC for 24 hours. Cool, open and discard the HF into the "waste HF" container provided. Rinse with H_2O. Proceed with the cleaning procedure as outlined for the Teflon beakers.

8.1.1.6 Cleaning microwave bombs

Between samples, fill the base and cap with 6M HCl^x and heat on a warmer for an hour. Discard acid and rinse with H_2O^x. Where better cleaning is necessary, one should then add 5 ml HF^x and 1 ml 15M HNO_3^x, seal in autoclave vessel and microwave for one minute. Cool for one hour, open and discard the HF into the "waste HF" container provided. Rinse with H_2O. Proceed with the cleaning procedure as outlined for Teflon beakers.

9 Sample weighing

Approximately 0.5 - 1.0 µg of Sr or Nd is required for a routine isotopic analysis. For most rock types, this can be achieved with 50-200 mg of rock powder. In older rocks, particularly those containing significant concentrations of mica, extremely fine grinding is required to achieve adequate homogeneity of the powder. In these cases, larger sample aliquots will need to be dissolved to achieve reproducibility. The ion-exchange columns are designed for 200 mg of an "average rock" (calculated on an average dolerite) and greater amounts should be divided prior to column separation to prevent overloading of the column.

Samples may be spiked for concentration measurements, or unspiked for isotopic composition determinations ("natural").

Before weighing into Teflon ware, leave the beakers on the anti-static mat with partially unscrewed caps for 2-3 hours. Also leave sample containers on the anti-static mat at the same time.

9.1 Calculating the required amount of spike for samples

In an analysis of the dependence of concentration error on constitution and concentration of 'tracer' or spike, Crouch and Webster (1963) demonstrated that error multiplication is minimised when:

$$M_{ij} = (S_{ij} * D_{ij})^{1/2}$$

From the equation for isotope concentration calculations (Section 18.1), it is simple to show that:

$$\text{Weight spike} = \frac{{}^{j}N * \text{weight sample}}{Q_D * {}^{j}S}$$

Where

$$Q_D = \frac{S_{ij} - M_{ij}}{M_{ij} - N_{ij}}$$

And

I,j are 'numerator' and 'denominator' isotopes in the ratio

S_{ij} is the enriched tracer or spike ratio

N_{ij} is the natural sample ratio

M_{ij} is the ratio of the sample and spike mix measured in the mass spectrometer

^{j}N is the concentration of the 'denominator' isotope in the sample

^{j}S is the concentration of the 'denominator' isotope in the spike

9.2 Weighing natural samples in beakers

1. Weigh 200 mg of sample powder into a static-free "Savillex" FEP vial or PTFE beaker, using the digital top-load balance. Tap beaker sharply on bench top to dislodge any sample powder clinging to the beaker sides.

9.3 Weighing concentration samples in beakers

1. Place a small glass beaker containing water into the balance housing prior to weighing. This retards the evaporation of spike solution from the Teflon beaker.

2. Tare static-free FEP vial or PTFE beaker on digital Mettler balance with the doors closed.

3. Weigh required amount of 84Sr spike solution into beaker. Allow balance to stabilise (wait for red "shake" indictor to disappear) and note the weight.

4. Tare the balance. Weigh required amount of 87Rb spike into beaker, allow balance to stabilise and note weight.

5. If Sm and Nd are to be determined on the same dissolution then: tare the balance; weigh required amount of mixed ^{149}Sm-^{150}Nd spike; allow balance to stabilise and note weight.

While working as carefully as possible, the above steps should be performed quickly to reduce weighing errors due to evaporation of the spike solutions.

6. Ensure that no droplets of solution are adhering to the beaker sides - the beaker may be lightly tapped to encourage droplets to slide to the beaker bottom. Dry down on hotplate in filtered air box. Allow to cool for at least 3 hours on the anti-static mat.

7. Tare beaker on balance. Weigh in required (ca. 200 mg) of sample powder, allow balance to stabilise and note weight. Carefully remove beaker and tap sharply on bench top to remove any powder adhering electrostatically to the sides. Replace on balance, allow to stabilise and compare weights.

9.4 Weighing natural samples in microwave bombs

1. Weigh 200 mg of sample powder into a static-free (as above) microwave digestion vessel, using the digital top-load balance. Tap beaker sharply on bench top to dislodge any sample powder held to the beaker sides.

9.5 Weighing concentration samples in microwave bombs

1. Remove all the extra metal sheets from beneath the balance pan. Do so very carefully.

2. Tare static-free PTFE vessel on digital Mettler balance with the doors closed.

3. Weigh required amount of ^{84}Sr spike solution into beaker. Allow balance to stabilise (wait for red "shake" indicator to disappear), and note the weight.

4. Tare the balance. Weigh required amount of ^{87}Rb spike into beaker, allow balance to stabilise and note weight.

5. Tare the balance. Weigh required amount of mixed ^{149}Sm-^{150}Nd spike, allow balance to stabilise and note weight.

While working as carefully as possible, the above steps should be performed quickly to reduce weighing errors due to evaporation of the spike solutions.

6. Ensure that no droplets of solution are adhering to the beaker sides - the beaker may be lightly tapped to encourage droplets to slide to the beaker bottom. Dry down on hotplate in filtered sir box. Allow to cool.

7. Tare beaker on balance. Weigh in required (ca. 200 mg) of sample powder, allow balance to stabilise and note weight. Carefully remove beaker and tap sharply on bench top to remove any powder adhering electrostatically to the sides. Replace on balance, allow to stabilise and compare weights.

10 Sample dissolution

Samples are normally dissolved in mixtures of concentrated HFx and HNO3x.

HF IS DANGEROUS

HF is an extremely dangerous and corrosive acid, forming fluorides in body tissues that are extremely difficult to displace. Furthermore, HF fumes, if inhaled, may cause irreparable lung damage. Disposable plastic gloves are provided and should be used whenever handling HF storage bottles or beakers containing HF. Before using this acid, read the available instructions on HF burns, and ensure that calcium gluconate ointment is available

Mixtures of HF and perchloric acids are more effective, but beware:

- **Perchloric acid forms explosive mixtures with organic materials.**
- **Perchloric is both difficult and dangerous to distil.**

Savillex beaker dissolution is effective for most common rock-forming silicates, but is not effective with refractory accessory phases like zircon or chromite. Neither phase will have any significant effect on Rb-Sr measurements, but the former is extremely important in rare earth studies (Sm-Nd). Samples for which complete dissolution is critical, should be processed using either microwave bombs or by fusion. Users are referred to the excellent book by Kingston and Jassie (1988) if they are interested in general microwave dissolution techniques, and to the paper by Vocke et al. (1987) for the fusion technique.

10.1 Rb-Sr silicate dissolution in beakers

1. Add 1-2 mlof concentrated (15M) HNO3x from the squirt bottle. Roll nitric acid around beaker bottom to thoroughly wet the sample powder. Ad 5 ml of HFx and swirl to mix acids and form a slurry with the sample. Allow initial violent reaction to subside. Cover with screw-on cap and allow to digest on warmer overnight. The sample should appear "waxy". If individual mineral grains are still discernible, evaporate to _ volume, add fresh HFx and 15M HNO3 and repeat.

2. Tap the Savillex beaker on the bench top to dislodge any droplets that may have collected on the inside of the cap. Rinse the inside of the cap with 1 m l 15M HNO3x from the squirt bottle and add this to the

sample. It is ***VERY IMPORTANT*** to make sure that the screw thread on the outside of the beaker is not touched at any state while processing the sample, as any contamination will then be transmitted to the screw thread on the inside of the beaker cap and thus to the sample when rinsing the cap with HNO3x.

10.2 Sm-Nd silicate dissolution in Parr microwave bombs

The Parr microwave bombs provide a very efficient yet simple method for the complete dissolution of inorganic samples. There are, however, a number of precautions which must be exercised when using Parr microwave bombs.

Never exceed 1 g of sample powder. If your sample contains organic components, DO NOT follow the procedure bellow. The presence of organics results in elevated vapour pressures very rapidly. If your sample contains organics, consult the Parr documentation After heating the bomb, allow it to cool completely, otherwise dangerous acid fumes may be vented onto you. The Parr design is intended to retain working pressures up to 1200 psi (~82 bar). Different acids generate different vapour pressures, as shown in Figure 1.

These pressures are attained very rapidly, so be careful. If the maximum pressure of the bomb's release disc is exceeded, the contents of the inner vessel will be ejected through the 4 small holes in the sides of the screw cap. Never look into these holes and wear protective clothing, gloves and eye covers when handling bombs which may still be hot or pressurised. If there is a sudden pressure release, the expulsion of gases through the 4 small holes will create a very loud noise, which may damage the hearing of people in the close vicinity.

Further details of the Parr microwave bombs, together with details of their operation and safety precautions to be followed, are provided in documentation supplied by Parr.

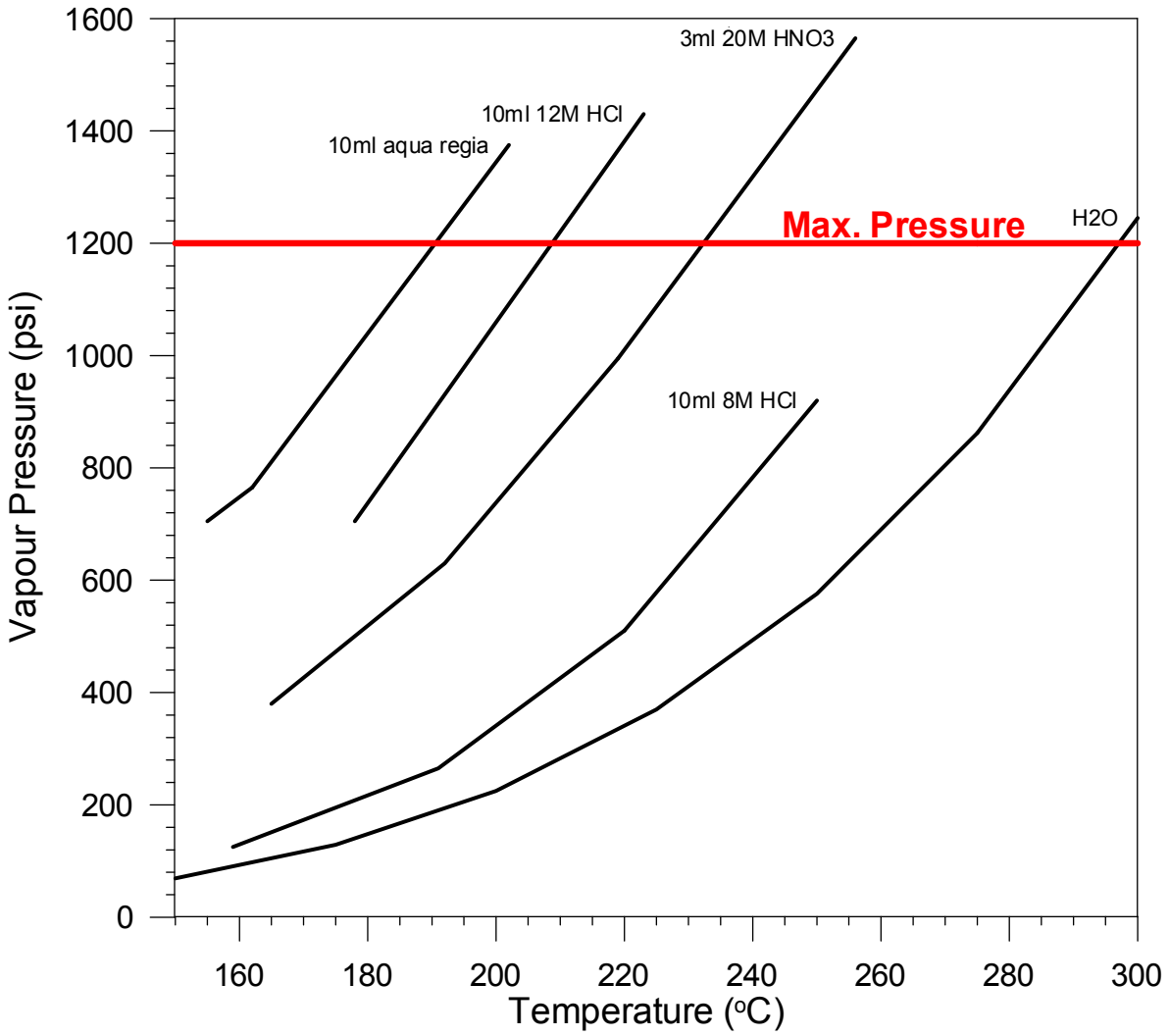


Figure 1. Variation of vapour pressure relative to temperature for different reagents in 23 ml Parr microwave digestion vessels. Curves are based on data provided by Parr Instrument Company.

1 Add 1 ml of conc. (15M) HNO_3^x from the squirt bottle. Roll nitric acid around autoclave bottom to thoroughly wet the sample powder. Add 5 ml of HF^x and swirl to mix acids and form a slurry with the sample. Leave open and heat on a hotplate. Allow to almost dry. This will drive off volatile silicate tetrafluoride and so reduce the likelihood of fluoride precipitates forming later. The sample should ***NOT*** dry completely at this stage, or fluorides will be extremely difficult to degrade. Fluorides will retain lots of REE and Sr (in CaF_2) and reduce final yields.

2 Add 1 ml of conc. (15M) HNO_3^x from the squirt bottle. Roll nitric acid around autoclave bottom to thoroughly wet the sample powder. Add 5 ml of HF^x and swirl to mix acids and form a slurry with the

sample. Use the top-load balance to get approximately correct amounts. Allow initial violent reaction to subside. Cover with top (with PTFE o-ring correctly in place). Insert into autoclave base and screw on cap until just finger tight. Note the weight for each assemblage. Place 4 bombs in microwave and switch on at full power for 2 minutes. ***Do not exceed this time period!!!*** Allow to cool for 1 hour then remove from oven and autoclave jacket.

3 Leave the bombs in the microwave oven for at least 10 minutes before touching. If necessary, e.g. top release the microwave oven for another batch of samples, remove after 10 minutes and place in a fume cupboard to continue cooling.

4 Cooling the bomb: The bomb must be completely cooled before attempting to remove the Teflon inner vessel. The body should be cool to the touch, and the head of the retaining screw should have retracted to its original position. For safety, allow 1 hour after heating for this to occur.

5 Weigh each Teflon assemblage to check for acid loss in the oven. Open the Teflon assembly. The sample should appear "waxy". If individual mineral grains are still discernable, evaporate to 1/3 volume, add fresh HF^x and 15M HNO_3^x (same quantities as before) and repeat.

6 Evaporate to 1/2 volume. Add 1-2 ml HNO_3^x. Repeat until volume of fluoride precipitate is reduced. The sample should ***NOT*** dry completely at this stage, or fluorides will be extremely difficult to degrade. Fluorides will retain lots of REE and Sr (in CaF_2) and reduce final yields.

7 Dry to 1/2 volume and add 2-3 ml of 6M HCl^x. Allow reaction to subside, then dry down. Add 2 ml 6M HCl^x and dry down. Add 5-8 ml 6M HCl^x, cover and let stand overnight on warmer. Check to see that dissolution is complete.

8 Dry down and cover ready for columns.

8.1.1.1 Microwave dissolution time calculation

Details in this section have been taken from Kingston and Jassie (1988).

8.1.1.2 Heat capacity of various reagents

Reagent	Molarity	C_P
HCl	12.0	0.5863
	6.0	0.7168
HF	28.9	0.6960
HNO_3	15.9	0.5728
	8.0	0.7162
H_2O	-	0.9997

8.1.1.3 Calculation of power absorbed by reagents

Ln (absorbed power) = A + B ln (mass) + C ln $(mass)^2$ + D ln $(mass)^3$ + E ln $(mass)^4$

Reagent	M	A	B	C	D	E
HCl	12	19.198223	-11.8319	3.42081805	-0.419341	0.01894251
	6	28.5892761	-20.2258	6.187086255	-0.806255	0.03845682
HF	29	36.4337146	-26.2649	7.91099431	-1.0178	0.04785757
HNO_3	16	27.1808917	-17.3782	4.9371303	-0.598649	1.02661368
H_2O	-	3.2003974	1.18320369	-0.160514	0.0079261	0.0

8.1.1.4 Time to reach final temperature

$$t = K C_P m (T_{final} - T_{start}) / P$$

where

K = conversion factor for thermochemical calories per second to watts

C_P = heat capacity in cal g^{-1} $^oC^{-1}$

m = mass in g

T_{final} = temperature in ^oC

T_{start} = temperature in ^oC

t = time in seconds

P = power absorbed in watts

One can determine the true power of a microwave oven by heating a known mass of water for a known period of time and determining the change in temperature of the water i.e. invert the above equation

The values provided by Kingston and Jassie (1988) are based on a 574 W microwave oven. To convert to another oven:

P_{new} = (new oven wattage) * P_{574} / 574

The times required to reach various temperatures for different reagents are illustrated in Figure 2 for a 574 W microwave oven. This diagram also illustrates the temperature at which PTFE melts but one must never approach this temperature. Figure 3 illustrates theoretical temperature vs pressure curves for different reagents and includes some which are not shown in Figure 1. Note, however, that some of the curves do not correspond well with experimentally determined curves of Figure 1.

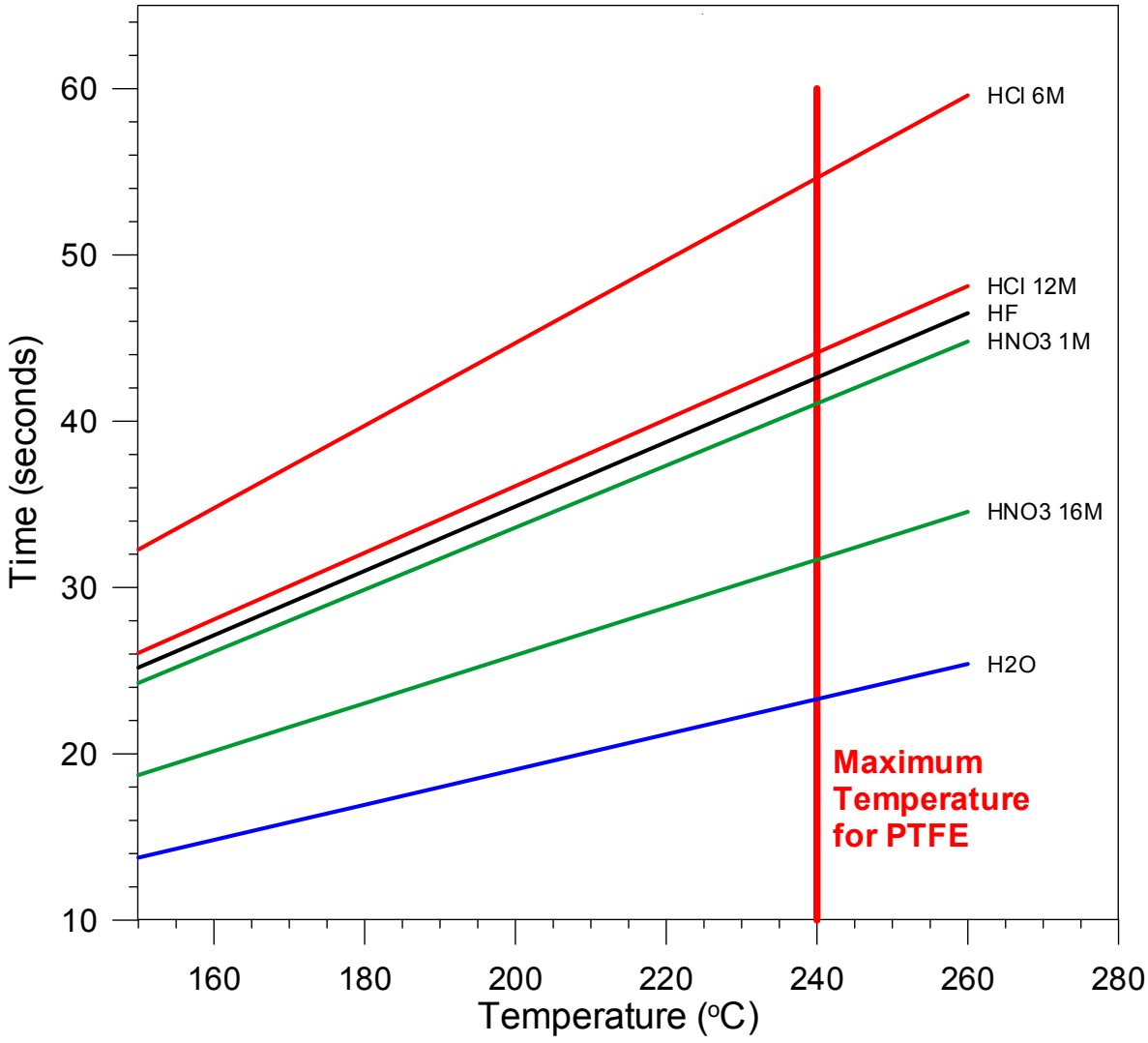


Figure 2. Time required to reach various temperatures for different reagents, base on theoretical values for the reagents. The melting temperature for PTFE is shown for comparative purposes only.

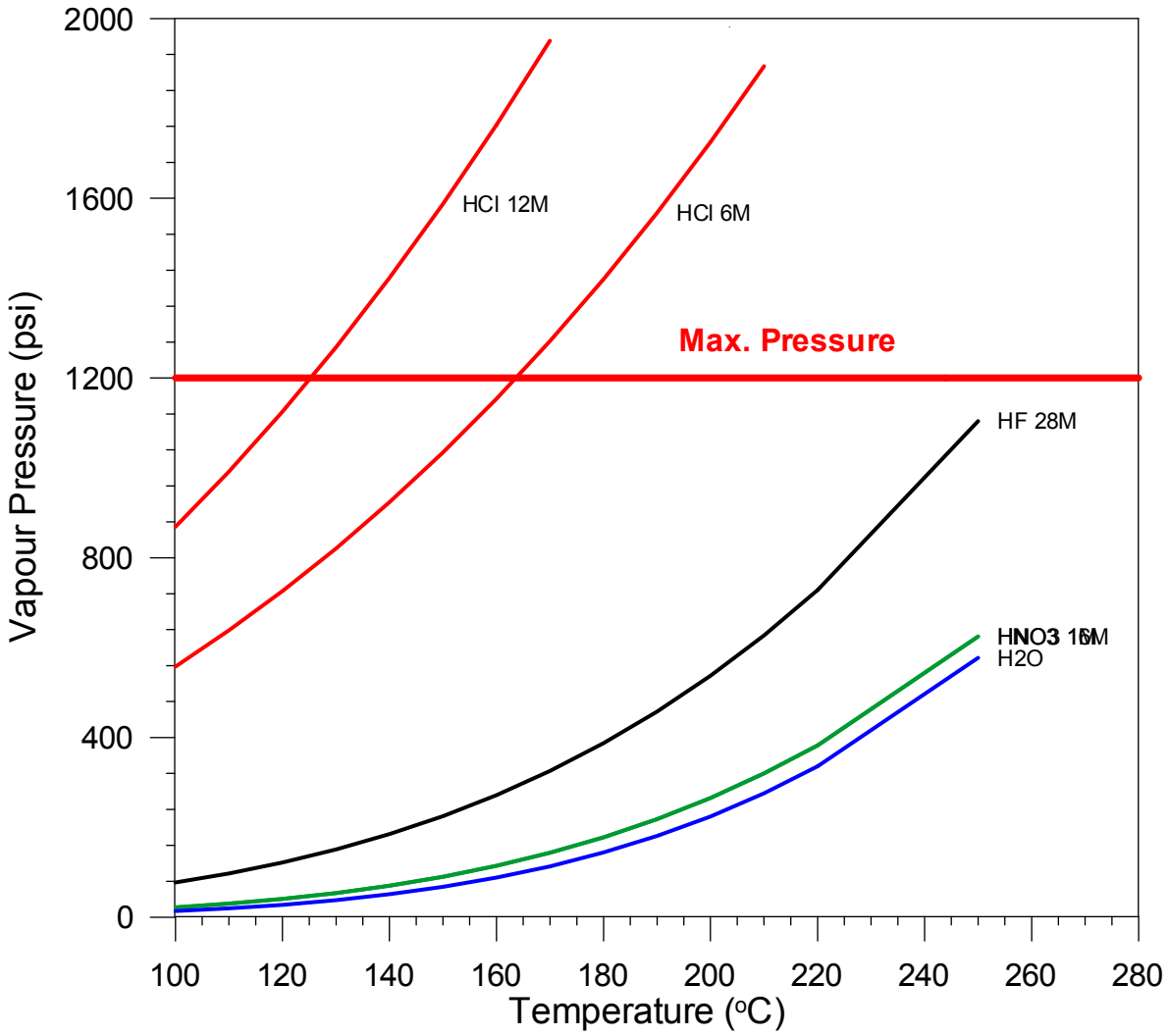


Figure 3. Variation of vapour pressure relative to temperature for different reagents. Curves are based on theoretical values for the reagents.

8.2 Use of the ultrasonic as a dissolution aid

8.3 Sample dissolution technique using $LiBO_2$ flux

The LiBO2 flux, used in the dissolution procedure outlined below, is commercially available (e.g. SPECTROFLUX made by Johnson Matthey Chemicals Ltd, and available from United Mineral and Chemical Corp, 129 Hudson Street, New York, NY 1003, Tel. 212-966-4330), or it can be by reacting boric acid (H3BO3) and lithium carbonate (Li2CO3) together in a platinum crucible (see Ingamells (1969) for details). In either case, the flux should be further purified by reprocessing as outlined below. The purpose of reprocessing is primarily to remove the excess reactants which will not readily go into solution in dilute acids. The presence of these unreacted constituents affects the yield of some elements during sample dissolution because of their tendency to scavenge cations of interest.

8.3.1.1 $LiBO_2$ preparation

This purification procedure is modified from Ingamells (1969). It is best to do the following steps, in either a clean lab or under a laminar flow hood. The procedure processes the LiBO2 in 200 g lots to yield approximately 130 g of purified powder, enough for more than 150 dissolutions.

1. In a 2 l container filled with distilled H2O, dissolve 200 g LiB(O2. Stir the solutions with a magnetic stirrer as the powder is added.

2. Heat the solution to 90oC with constant stirring for approximately 1 hour.

3. Cool the solution to 85oC, again with constant stirring for approximately 1 hour.

4. Filter the solution immediately and as rapidly as possible into another 2 l container.

5. Cover and leave filtrate in a cool place for at least 48 hours without stirring.

6. Pour off the supernatant.

7. Heat the crystals of lithium metaborate (now an octahydrate) to approximately 45oC in a ventilated oven until they are reduced to a dihydrate. They will turn a chalky white colour. Do not heat the crystals above 45oC as they may react with the container.

8. Transfer SMALL amounts of the dihydrate to Pt dishes and bring then slowly up to approximately 625oC for 1 hour in a suitable furnace. This reaction is accompanied by a large volume increase.

9. Grind the LiBO2 in an agate mortar, sieve with a nylon mesh to 80 mesh, and mix well. The flux is now ready for use.

Table 1 REE total blank values in picograms (1983, Mineralogical Institute, Basel) for different sample dissolution techniques (includes column chromatography)

Element	Flux dissolution1	HF dissolution2
Ce	1122	586
Nd	369	177
Sm	66	6
Eu	15	1
Gd	66	
Dy	67	20
Er	43	10
Yb	42	30

1. Flux dissolution - Graphite crucible, flux, inorganic and organic acids.
2. HF dissolution - Teflon bomb, inorganic and organic acids.

8.3.1.2 Sample dissolution with $LiBO_2$ flux in graphite crucibles

This dissolution was originally used for atomic absorption analyses by Suhr and Ingamells (1966). The graphite crucible technique given here, is a modification of a Pt-crucible technique developed by R Hänny at Sony Brook for whole rock REE analyses. The graphite crucibles we are currently using are the Ultra-Carbon Graphite Crucibles, Type 818004, Grade UF-45, also available from Johnson Matthey Chemicals Ltd. The selection and handling of the crucible are quite important for low REE blank levels. The REE total blank levels listed in Table 3, however, attest to the lack of REE contaminants in either the flux or the graphite crucibles with careful handling during routine analyses.

A muffle furnace, capable of sustained temperatures around 1,100□C, graphite crucibles, Teflon coated magnetic stirring rods, Teflon beakers 100 ml size), Teflon watch glasses, magnetic stirring plate, and long handled tongs for manipulating the crucibles into and out of the furnace are needed for this process. The graphite crucibles may be reused for successive dissolutions with no detectable memory effects, provided a uniform portion of the interior is scraped out with an appropriate tool before reuse. Furthermore, degradation of the crucible walls, due to oxidation, can be reduced by covering the individual crucibles with miniature quartz glass bell jars with ground glass rims which form a seal with a ground quartz glass floor in the oven. This also eliminates any chances of cross contamination of samples. The quartz glass bell jars can be cleaned in acids, together with the Teflon-ware, between analyses.

1. Carefully wipe the interior of the graphite crucibles to remove any foreign material, and deeply score the outside with a number, letter or identifying mark, in order to keep samples distinct.

2. Pre-ignite the crucibles in the furnace at 800□C for 5 minutes. After they cool, tap then lightly to remove any loose graphite and cover them with a cap made from aluminium foil.

3. Weigh approximately 800 mg of purified LiBO2 directly into the crucible. A beam balance can be used for this weighing, as the exact amount of flux is not important. Make a small pocket in the centre of the powder to receive the sample powder later. Cover with the aluminium foil cap.

4. Accurately weigh out approximately 20 mg of sample powder (at -200 mesh) on an analytical balance, and add to the appropriate crucible. Mix the powder thoroughly with the flux. Recap the crucibles.

5. With the muffle furnace at around 600□C, remove caps from crucibles and place them inside. Cover each sample with a quartz glass bell jar. Bring the temperature up to 1,050□C over a period of about 15 minutes and hold at this temperature for a total period of 30 minutes.

6. Clean as many 100 ml Teflon beakers, Teflon watch glasses and magnetic stirrers as there are graphite crucibles.

7. Add 30 ml of 1N HNO3 for REE analysis (or 30 ml of 1N HCl for Rb - Sr analysis) and the magnetic stirrers to the beakers.

8. Add a known amount of spike to the acid solutions in the beakers.

9. Gently heat the spiked beaker with watch glass in place until the crucibles are to be removed from the furnace.

10. Remove the graphite crucibles from the furnace, swirling each to collect any separated droplets. Rapidly pour the molten sample into the appropriate beaker, immediately capping it with the watch glass.

11. Place the beaker on the magnetic stir plate and mix for at least 2 hour. The samples are now ready for column chromatography.

The cation exchange columns should be in the proper molarity acids and have cleaned funnels with disposable frits or filter paper in place ready to receive the solutions. The solutions are then poured into the funnels and loaded directly onto the columns. Filtering is necessary to remove graphite and a minute quantity of crystals that form in the solution. The total time between the start of this operation and loading samples onto the columns is around 1 hour.

8.4 Carbonate dissolution

Carbonatites, marbles, etc. are composed primarily of calcite (CaCO3) and dolomite (Mg-CaCO3), which are readily soluble in weak acids such as HCl. Some samples, however, contain small concentrations of silicate minerals which require dissolution in HF. Adding HF directly to the sample will form CaF2 (fluorite), which is insoluble in HCl and very difficult to break down. A 2-stage dissolution procedure is therefore used.

1. Weigh required amount of carbonate rock powder into beaker.

2. Wet powder with a small amount of H2Oxrx (~1-2 ml).

3. Slowly add ~2 ml 2.5M HClx to beaker, and allow reaction to subside. Add 2 more 2 ml aliquots of the acid and parafilm the beaker.

4. After 2-3 hours, check to see whether any residue remains. Dry down slowly.

5. Add 4 ml 6M HClx and warm gently.

6. If residue is present, then swirl solution to mix and pour into a cleaned 5-10 ml polypropylene centrifuge tube. Rinse beaker with a small amount of 6M HClx and add to centrifuge tube. Centrifuge for 10 minutes at 4000 rpm.

7. Decant supernate into a new beaker and wash residue into original beaker with 6M HClx. Dry down both beakers.

8. Add 1 ml HFx to beaker containing the residue, cover and allow to stand until dissolved. Add 1 mlHNO3x conc. and dry down. Repeat until brown and dissolve in 6M HClx.

9. Combine contents of both beakers and dry down.

10. Continue with column procedure as normal.

In other cases, it is only necessary to extract the Sr component from the carbonate fraction, not from the silicate impurities accompanying the carbonates. In this case, there are several alternative techniques which may be adopted according to the exact requirements of the study. These are given below.

8.4.1 Nitrate precipitation of Sr

8.4.1.1 Reagents required:

5 N acetic acid

dilute nitric acid

concentrated nitric acid

clean water.

8.4.1.2 Method:

1. Place ~100 mg of carbonate sample in polypropylene micro-centrifuge tube.
2. Add ~1.5 ml 5N acetic acid.
3. Ultrasonic for 1 hour.
4. Centrifuge
5. Pour supernate into another micro-centrifuge tube.
6. Dry in hotplate under heat lamp.
7. Add a few drops of dilute nitric acid.
8. Top up with 90% concentrated nitric acid.
9. Ultrasonic.
10. Pipette off supernate.
11. Add a few drops of dilute nitric acid.
12. Top up with 90% concentrated nitric acid.
13. Ultrasonic.
14. Pipette off supernate.
15. Add a few drops of dilute nitric acid.

16. Add 1 ml 90% concentrated nitric acid.

17. Ultrasonic.

18. Pipette off supernate.

19. Dissolve precipitate with dilute nitric acid and transfer to small Teflon beaker or planchette.

20. Dry sample in preparation for mass spectrometer.

8.4.2HCl dissolution with cleaning of specimen

8.4.2.1 Reagents required:

0.2M HCl

0.4M HCl

clean water

2.5M HCl

8.4.2.2 Method:

1. Place ~100 mg of carbonate sample in Teflon planchette.

2. Cover with 0.2M HCl for ~5 minutes.

3. Rinse with clean water.

4. Transfer to clean polypropylene micro-centrifuge tube. Remove top from tube. Add 0.4M HCl and cover tube with parafilm.

5. Ultrasonic for 1 hour.

6. Centrifuge.

7. Pour supernate into clean Teflon beaker.

8. Dry on hotplate under heat lamp.

9. Proceed to standard Sr natural cation column process.

10. Dry sample in preparation for mass spectrometer.

8.4.3HCl dissolution without need for cleaning of specimen

8.4.3.1 Reagents required:

2.5M HCl.

8.4.3.2 Method:

1. Place ~100 mg of carbonate sample in Teflon beaker.
2. Add ~1.8 ml 2.5M HCl. Allow to stand for 24 hours.
3. Transfer to clean polypropylene micro-centrifuge tube.
4. Centrifuge.
5. Proceed to standard Sr natural cation column process.
6. Dry sample in preparation for mass spectrometer.

8.4.4Acetic acid dissolution with cleaning of specimen

8.4.4.1 Reagents required:

5 N acetic acid

clean water

2.5M HCl

6M HCl.

8.4.4.2 Method:

1. Place ~100 mg of carbonate sample in Teflon planchette.
2. Cover with 5 N acetic acid for ~5 minutes.
3. Rinse with clean water.
4. Transfer to clean polypropylene micro-centrifuge tube. Remove top from tube. Add 5N acetic acid and cover tube with parafilm.
5. Ultrasonic for 1 hour.
6. Centrifuge.
7. Pour supernate into clean Teflon beaker.

8. Dry on hotplate under heat lamp.

9. Add ~15 ml of 6M HCl.

10. Dry on hotplate under heat lamp.

11. Proceed to standard Sr natural cation column process.

12. Dry sample in preparation for mass spectrometer.

8.4.5Dilute HCl dissolution without cleaning of specimen

8.4.5.1 Reagents required:

0.2M HCl or 0.4M HCl

2.5M HCl.

8.4.5.2 Method:

1. Place ~200 mg of carbonate sample in polypropylene centrifuge tube.

2. Remove top from tube. Add 0.4M HCl and cover tube with parafilm.

3. Ultrasonic for 1 hour.

4. Centrifuge.

5. Pour supernate into clean Teflon beaker.

6. Dry on hotplate under heat lamp.

7. Proceed to standard Sr natural cation column process.

8. Dry sample in preparation for mass spectrometer.

8.5 Dissolution of anhydrite samples for Sr isotope analysis

Anhydrites are particularly difficult to dissolve but do contain substantial Sr concentrations (typically > 500 ppm). The best way to dissolve anhydrites seems to be in cold water (solubility product is 0.209 g per 100 ml in cold water whereas the solubility product is only 0.16 g per 100 ml in warm water). The recommended procedure is thus:)

1. Determine the amount of anhydrite require in order to have at least 1 μg Sr for analysis. If the concentration in the sample is unknown, assume 500 μg/g.

2. Weigh the required amount of sample into a 50 ml Savillex beaker.

3. Add a few ml of 6M HCl and dissolve any carbonate present in the sample.

4. Dry on a hotplate.

5. Cool and add sufficient cold Millipore water to dissolve the sample i.e. (weight sample in g / 0.209) * 100 ml.

6. Ultrasonic occasionally over a period of 2 days.

7. Dry and then take up soluble portion in HCl ready for centrifuging prior to cation column separation.

8.6 Pb-Pb silicate sample dissolution

The method is designed for 200 mg samples. If problems of sample inhomogeneity are expected, larger aliquots may be dissolved. However, the sample must then be divided accordingly before column separation.

Sample dissolution (except for samples containing important refractory accessory phases, such as zircon) is done in 15 ml Savillex beakers. Five sets of eight 15 ml Savillex beakers are available for use. These are labelled A1 - A8, B1 - B8, etc. Before commencing Pb analyses on a batch of samples, a set of 8 beakers (e.g. A1 - A8) may be drawn from the store. These must be cleaned in the conventional way before use (24 hours in hot conc. HNO3GR, followed by 24 hours in hot H2Oxrx, rinsing in H2Oxr in between).

Follow the same dissolution procedure as set out for the Rb-Sr method until the drying down stage, which is as follows:

Evaporate to 2 volume and add another ml of 15M HNO3x. Evaporate until the sample is a sludge in the bottom of the beaker, add 1 ml 15M HNO3x and dry down. Cover and allow to cool. The sample is now ready for the columns.

For samples containing important refractory accessory phases, such as zircon, the sample may be dissolved in one of two ways:

1. Dissolve sample in conc. HNO3x/HFx in a Savillex beaker, seal and leave to digest overnight on the warmer. Evaporate to _ volume, add fresh HNO3x and HFx, seal and leave to digest on the warmer for 2-3 days. Follow the procedure for drying down described above.

2. Dissolve sample in conc. HNO3x/HFx in a Teflon microwave bomb. Dry down as described above.

Four samples are processed at a time. Samples are put through 2 column separations. This eliminates the necessity of purifying the Pb by electro-deposition. The Pb from the first column separation is collected into the

same Savillex beakers used for sample dissolution, after they have been cleaned. The purified Pb from the second column separation is collected into a new clean set of Savillex or PTFE beakers.

Add approximately 1 ml 0.5M HBrrr to each sample. Seal and leave to dissolve for approximately 15 minutes. Take four 1.9 ml polypropylene centrifuge tubes from the storage container. (Wear plastic gloves when doing this.) Shake off as much of the excess water as possible. Rinse the centrifuge tubes with 0.5M HBrrr. Label and transfer the sample to the centrifuge tube, making sure that any undissolved "sludge" in the bottom of the beaker is transferred. Rinse the beaker with approximately 0.5 ml 0.6M HBrrr and transfer it to the centrifuge tube. Seal and place in the small ultrasonic for approximately 2 minutes. This facilitates the leaching by HBr of any remaining Pb in the undissolved sample. Transfer to the centrifuge and centrifuge at 4000 rpm for 10 minutes.

Rinse the Savillex beakers and caps carefully with H2Oxrx and place approximately 1 ml 0.5M HBrrr in the bottom of each beaker. Seal tightly and place on the Salton warmer to flux. Just prior to Pb collection, remove from the warmer, discard the HBr and rinse thoroughly with H2Oxrx. The beakers are now ready for Pb collection.

8.7 Mineral dissolution

8.7.1 Dissolution of fluorite

8.7.1.1 H_2SO_4 method

1. Place 50 - 100 mg fluorite in 100 m Teflon wide-mouthed evaporating dish.

2. Add 1 - 2 ml 18M H2SO4 and 0.1 ml 16M HNO3.

3. Keep mixture at 150□C for several hours until digestion is complete and fluorite is converted to a white slurry. Add more H2SO4 as necessary.

4. Increase temperature to about 220□C and evaporate to half volume.

5. Cool and add 2 - 7 ml 2.5M HCl. Add drop by drop to minimise strong exothermic reaction.

6. After the white precipitate is dissolved (1 - 12 hours), increase the temperature to about 220 □C to evaporate the excess HCl and H2SO4.

7. Remove evaporating dish from heat source when fuming is complete. Do not dry completely as subsequent dissolution becomes very difficult.

8. Take back into solution with warm water and aliquot as necessary for spiking and analysis.

8.7.1.2 H_3BO_3 Method

Sampling, preparation and dissolution procedures for the fluorite study, described in Eppinger and Closs (1990), are described below.

Sampling and preparation procedures

Fluorite crystals or cleavage fragments free of iron oxide straining or other mineral encrustations were selected.

Rock preparation began with crushing and coarse-grinding. Coarsely-ground fractions were sieved and the minus-10-mesh (1,7 mm) to plus-35-mm (0,4 mm) fraction was saved for further preparation and analysis. This size fraction was used because grains larger than 10-mesh were commonly not mono-mineralic and grains smaller than 35-mesh were difficult to identify microscopically with certainty. The samples were gravity separated using bromoform (specific gravity 2,85; fluorite sinks) and the heavy fractions were then separated with a Frantz electromagnet (fluorite is non-magnetic). The non-magnetic heavy fractions were examined using a binocular-microscope and fluorite grains were hand-picked for further preparation.

The fluorite grains were cleaned using an ultrasonic vibrator in demineralized water for 30 minutes, to clean cleavage recesses and to remove loosely adhered surficial coastings, clay and other grains adhered to the fluorite by static electricity. The samples were next examined microscopically with short- and long-wave ultraviolet light to remove grains containing foreign fluorescing mineral inclusions such as scheelite and willemite. As a final check for purity, the fluorite grains were scanned with a low-power petrographic microscope. Trace anisotropic minerals and fluorite grains containing abundant anisotropic mineral inclusions were removed. X-ray diffractometry was used to ascertain purity of the fluorite separates. Finally, the fluorite samples were weighed and hand=ground for chemical analysis using an agate mortar and pestle. Clean quartz sand was ground between each sample to minimize contamination. The fluorite samples were estimated to be at least 99 % pure CaF2.

Sample Digestion

The fluorite dissolution procedure used is a modification of brief descriptions of the topic by Dolezal et al. (1968) and Feigl (1958, p 270-271), the latter stating that "in the presence of small amounts of acid, precipitated or native calcium fluorite is readily soluble in warm aqueous solutions of salts that form complex fluorides." Salts mentioned include those of aluminium, beryllium, boron, chromium and iron. Both Dolezal et al. (1968) and Feigl (1958) suggest the use of either perchloric or hydrochloric acid in the dissolution procedure. The mechanism for fluorite dissolution is relatively simple: the salt dissociates in the acid, aqueous solution and the salt cation complexes with fluorine. Since the complex ion is more stable than fluorite in the solution, fluorite dissolves. Warming the solution speeds up the reaction.

Substitutions were necessary for the reagents recommended by Dolezal et al. (1968) and Feigl (1958) as these reagents are not compatible with the ICP-MS method. Salts were not used because high salt content in the sample matrix causes interference problems with the ICP-MS method (Van Loon and Barefoot, 1989). Boron was selected as the complexing cation and a 5000 □g/ml boron standard (as boric acid in demineralized water) was used in lieu of a boron salt. Chloride ions form numerous complexes with REE. Thus, nitric acid was used instead of hydrochloric or perchloric acids.

Using these reagents, boron (as B3+) complexes with fluorine, forming the fluoroborate ion, BF4. Qualitatively, the reaction is:

$$2CaF_2 + B^{3+} < --- > 2Ca^{2+} + BF_4^-$$

Since the REE substitute for calcium in fluorite, the above reaction puts the REE into solution. After experimentation[1], the following procedure was selected for fluorite dissolution:

[1] Note: If problems with fluorite staying in solution are encountered, try
(1) analyzing the solutions while still warm, or

1. Weight 0.100 0.001 g CaF2 power.

2. Add 0.50 ml concentrated HNO3.

3. Add 3.0 ml 500 □g/ml B standard.

4. Heat to 90 □C for 10 minutes.

5. Cool to room temperature' cap and let sit for 24 hours.

6. Add 3.0 ml 500 □g/ml B standard.

7. Heat to 90 □C for 4 hours.

8. Let cool to room temperature.

9. Add 1.0 ml 5 □g/ml Th + 5 □g/ml Cd standards[2]

10. Bring solution up to 10.0 ml with de-mineralized water.

11. Cap/agitate.

12. Analyze solution.

The following reagents were used in the dissolution procedure: Baker "instra-Analyzed" concentrated nitric acid (70.0-71.0 %) for Trace Element Analysis, Titrisol 5000 □g/ml boron standard as H3BO3 in de-mineralized water, SPEX Industries 1000 □g/ml cadmium standard in 2 % HNO3 diluted to 5 □g/ml with de-mineralized water and SPEX Industries 1000 □g/ml thorium standard in 10 % HNO3 diluted to 5 □g/ml with de-mineralized water. The cadmium and thorium internal standards are used to monitor/correct for sensitivity variation and changes in metal-to-metal oxide ion ratios, respectively (Lichte and others, 1987). The dilution factor is 1:100, as shown below:

(0.100 g CaF2)/(10.0 ml solution) = 1/100.

8.8 Sulphide mineral dissolution

Basic dissolution procedures on published techniques for sulphide mineral separation and analysis (Neuerburg, 1975; Ho *et al.*, 1994).

---

(2) using a saturated boron solution, rather than a 500 µg/ml boron standard.

[2] A revised method currently utilized by USGS laboratories uses the following internal standards: 0,1 ml 20 µg/ml ln, 0,1 ml 20 µg/ml Lu, and 0,1 m 100 µg/ml Th, all in a 1 % HNO_3 solution. Thus Lu is not included in the current REE determination suite.

- Weigh a fragment of sample in disposable plastic beaker (beaker 1) and rinse with Milli-Q water.
- Decant the Milli-Q water
- Add 10 ml of acetic acid, cover the beaker with parafilm and allow to stand overnight. This will dissolve calcite in the sample.
- Decant the acid into another disposable beaker (beaker 2).
- Add more acetic acid to beaker 1 and allow to stand for 2 days with occasional periods in an ultrasonic.
- Transfer this acid to beaker 2.
- Dry acid in beaker 2, cool and add the requisite spikes e.g. Rb, Sr
- Add 6M HCl^X to the sample in beaker 1 and allow to stand covered for 1 week. *Do not heat or ultrasonic the sample*. Regularly swirl the beaker contents.
- Decant acid into a new, clean, disposable beaker (beaker 3). Rinse the sample with Milli-Q water and add to acid in beaker 3. Dry the solution before covering the beaker with parafilm. This beaker can now be prepared for Pb isotope analysis of pyrrhotite.
- Add concentrated HF^X to the sample in beaker 1 and allow to stand covered in a safe place for 2 weeks. *Do not heat or ultrasonic the sample*. Regularly swirl the beaker contents.
- Decant acid into a new, clean, disposable beaker (beaker 4) and dry this solution before covering the beaker with parafilm.
- Repeat the last two steps until little or no obvious undissolved silicate material remains.
- Rinse the sample thoroughly with Milli-Q water and add to beaker 3.
- Dry the solution in the beaker and allow it to cool. Redissolve contents of this beaker with 3M HNO_3 (not weight of acid used) and split into two aliquots (note weights). Prepare one aliquot for Rb-Sr and Pb isotope analysis and the other for Rb, Sr, U, Th, Pb concentration analysis by ICPMS. Add the requisite spikes to the aliquot for isotope analysis e.g. Rb, Sr. These analyses will provide an indication of the isotopic composition of the silicate rock which hosts the mineralisation.
- Add 1M dibasic ammonium citrate to sample in beaker 2 and leave for 2 days with occasional swirling. This step removes water-insoluble fluorides that tend to form gels with Al in the final digestion.
- Discard the ammonium citrate solution and thoroughly rinse with Milli-Q water. Discard the water used.
- Add 6M HCl^X to the sample and allow to stand covered for two days with occasional swirling. This step removes any citrate crystal which may have formed.
- Repeat the last three steps until a clean sulphide separate is obtained.
- Thoroughly rinse the sample with Milli-Q water then add 1M aluminium chloride and allow to stand for one day.

- Rinse sample thoroughly with Milli-Q water, then with a small amount of acetone to remove the water.
- Leave sample to dry in covered beaker.
- Weigh the sulphide minerals recovered and relate this to the original weight of sample.
- Hand picking of specific phases may now be performed.

Step	Analyse for	Acetic acid	2.5M HCl	HF	6M HCl	HNO3
1	Sr	calcite				
3	Pb		dolomite		sphalerite pyrrhotite stibnite cuprite	
						chalcocite bornite galena chalcopyrite troilite arsenopyrite molybdenite bournonite
2	Sr, Pb			silicates		

8.9 Solubilities of selected sulphide and oxide minerals

Table 2. Sulphide Mineral Solubilities and Magnetic Properties

Mineral	Solubility				Magnetic
	HCl	HNO_3	Aqua Regia	HF cold	
chalcocite		soluble		insoluble	
bornite		soluble (blue solution)		insoluble	
galena		soluble in dilute acid (may release H_2S)		soluble	
sphalerite	slowly soluble (releases H_2S)			insoluble	
chalcopyrite		soluble (green solution)			no
pyrrhotite	soluble (releases H_2S)	poorly soluble			yes
troilite		soluble			no
pyrite	insoluble		soluble	insoluble	no
stibnite	slowly soluble			insoluble	
marcasite				insoluble	
arsenopyrite		decomposes (insoluble		insoluble	

		sulphur)			
molybdenite		soluble	soluble	insoluble	
bournonite		soluble (pale blue-green solution)			
cuprite	soluble (blue solution)				
hematite	slowly soluble in hot, concentrated acid (intense reddish-yellow solution)				
cassiterite	insoluble	insoluble		insoluble	
magnetite	very slowly soluble in hot acid			soluble	yes
gold			soluble	insoluble	

8.10 Solubility characteristics of minerals

HCl - hydrochloric (muriatic) acid
HNO_3 - nitric acid
H_2SO_4 - sulphuric acid (oil of vitriol)
HF - hydrofluoric acid
AR - aqua regia (a mixture of hydrochloric and nitric acids
xx - easily dissolved and damaged
x - moderately dissolved and damaged
x - difficultly dissolved and slightly damaged
o - not affected

table to insert here

9 Column separations

9.1 Column types available

Various sets of columns may be used:

1. 6 ml of Bio-Rad AG50Wx12, 200-400# cation resin packed in a 10 mm ID quartz glass column which is used to separate Rb, Sr and the bulk REE fraction;

2. 6 ml of Bio-Rad AG50Wx8, 200-400# cation resin packed in a 10 mm ID quartz glass column which is used to separate the bulk REE fraction using 2.5M HCl and 3M HNO3;

3. 3 ml of Bio-Rad AG50Wx8 cation resin packed in a quartz glass column which is used to separate the bulk REE fraction using 0.1M Oxalic acid and 1M HCl, followed by 2M HNO3 and 6 M HCl;

4. 2.5 ml of Teflon/HDEHP reverse-phase ion exchange packed in an 8 mm ID quartz glass column which is used to extract pure Nd and Sm fractions from the bulk REE fraction;

5. 40 □l of Bio-Rad AG1x8 anion resin in miniature quartz glass columns used to separate Pb and U from other elements.

The Teflon/HDEHP ion exchanger is hydrophobic and, unlike the cation resin columns, particular care should be exercised when using these columns not to allow the ion exchanger to become dry (see later).

Preparation and calibration procedures for these columns are described elsewhere.

9.2 12% cation columns

1. Check log that the columns have been cleaned (90 ml each of 6M HClx and H2Oxrx) and equilibrate with 30 ml of 2.5M HClx. During wash/equilibration stage, the initial amounts of solution should be added carefully to the column using squirt bottle, rinsing the insides of the column. At the end of the quilibration stage no resin particles should remain in the reservoir part of the column and the upper surface of the resin bed should be flat. Waste HCl collected from the columns at this stage should be put in the container provided and not flushed down the sink.

2. Dissolve sample in 1-2 ml of 2.5M HClx (do NOT warm the solution as this will change the acid molarity), transfer to cleaned and numbered 1.9 □l microcentrifuge tubes. Evenly distribute the tubes in the centrifuge and run at 4000 rpm for 10 mins.

3. Load 1 ml of supernate from 2 onto top of resin bed with micro-pipette taking care to disturb the upper surface of the bed as little as possible. Allow sample to sink into the resin completely. Be sure to use a new pipette tip for each sample!!! Rinse beaker with 6M HClx and H2Oxrx to remove any traces of undissolved sample, half fill with 6M HClx, close and stand on warmer tray in filter unit.

4. Wash sample into resin with two 1 ml aliquots of 2.5M HClx, rinsing the column sides carefully. Allow first wash to sink in completely before adding the next. For efficient column separations the sample load should enter the resin bed in as small a volume of solution as possible: care must be exercised not to wash sample off the top of the resin bed when adding the wash solutions.

5. Follow the column log to separate Rb and Sr (if required). The first 3 ml of each new addition of acid should be applied with the pipettor, taking care not to disturb the resin. The REE fraction (if required) is stripped from the column with 6M HClREE. Where the HCl has been contaminated by iron (indicated by the yellow colour of the acid), wash the acid down the sink with copious amounts of running water otherwise place in the waste HCl container provided. The Sr fraction from unspiked samples may be collected in the original beaker, thoroughly cleaned as described in 3 above. Discard HCl when the beaker is needed and rinse thoroughly with H2Oxrx. Fresh beakers should be used for collecting Sr from Rb-rich samples and spiked dissolutions (the original beaker is used to collect Rb in the latter case).

6. Dry down collected fractions. Add 1 drop 1M HNO3x to the Sr fraction and dry down. Rb, Sr now ready for mass spectrometric analysis.

9.3 8% cation columns - HCl and HNO_3

1. Check log that the columns have been cleaned (90 ml each of 6M HClx and H2Oxrx) and equilibrate with 30 ml of 2.5 HClx. During wash/equilibration stage, the initial amounts of solution should be added carefully to the column using a squirt bottle, rinsing the insides of the column. At the end of the equilibration stage no resin particles should remain in the reservoir part of the column and the upper surface of the resin bed should be flat. Waste HCl collected from the columns at this stage should be put in the container provided and not flushed down the sink.

2. Dissolved sample in 1-2 ml of 2.5 HClx (do NOT warm the solution as this will change the acid molarity), transfer to cleaned and numbered 1.9 □l microcentrifuge tubes. Evenly distribute the tubes in the centrifuge and run at 4000 rpm for 10 mins.

3. Load 1 ml of supernate from 2 onto top of resin bed with micropipettor taking care to disturb the upper surface of the bed as little as possible. Allow sample to sink into the resin completely. Be sure to use a new pipette tip for each sample!!! Rinse beaker with 6M HClx and H2Oxrx to remove any traces of undissolved sample, half fill with 6M HCl, close and stand on warmer tray in filter unit.

4. Wash sample into resin with two 1 ml aliquots of 2.5M HClx, rinsing the column sides carefully. Allow first wash to sink in completely before adding the next. For efficient column separations the sample load should enter the resin bed in as small a volume of solution as possible: care must be exercised not to wash sample off the top of the resin bed when adding the wash solutions.

5. Follow the column log, changing reagent as necessary. Each new addition of acid should be applied with the pipettor, taking care not to disturb the resin. Where the HCl has been contaminated by iron (indicated by the yellow colour of the acid), wash the acid down the sink with copious amounts of running water otherwise place in the waste HCl container provided.

6. Dry down collected fractions.

7. Add 1 ml 2.5M HClx to each fraction and dry down.

9.4 8% cation columns -oxalic acid and HCl

1. Check log that the columns have been cleaned (90 ml each of 6M HClx and H2Oxrx) and equilibrate with 30 ml of the oxalic acid-HCl mixture. During the wash/equilibration stage, the initial amounts of solution should be added carefully to the column using a squirt bottle, rinsing the insides of the column. At the end of the equilibration stage no resin particles should remain in the reservoir part of the column and the upper surface of the resin bed should be flat. Waste acid collected from the columns at this stage should be flushed down the sink.

2. Dissolve sample in 2 ml of acid mixture (do NOT warm the solution as this will change the acid molarity) and transfer to cleaned and numbered centrifuge tubes. Evenly distribute the tubes in the centrifuge and run at ~4000 rpm for 10 mins.

3. Load 2 ml of supernate from 2 onto top of resin bed with micropipettor taking care to disturb the upper surface of the bed as little as possible. Allow sample to sink into the resin completely. Be sure to use a new pipette tip for each sample!!!

4. Wash sample into resin with two 1 ml aliquots of acid mixture, rinsing the column sides carefully. Allow first wash to sink in completely before adding the next. For efficient column separations the sample load should enter the resin bed in as small a volume of solution as possible: care must be exercised not to wash sample off the top of the resin bed when adding the wash solutions.

5. Follow the column log to separate the bulk REE. The first 3 ml of each new addition of acid should be applied with the pipettor, taking care not to disturb the resin.

6. Dry down collected fractions.

9.5 Alternative REE Bulk Separation

12.5 ml Col AG50W-X8 200-400#

elution sequence: Mg, Ca, Sr, Ba, HREE-LREE, La

Nd, Sm purification

AG1-X4 200-400#

0.06 M HNO3/85% MeOH

Require 0.4 M HNO3 stock solution

15% 0.4 M + 85% MeOH = 0.06 M HNO3/MeOH

9.6 LN columns

The Teflon/HDEHP resin is extremely hydrophobic and should NEVER be allowed to dry otherwise the adjacent HDEHP-coated particles will weld, sealing off porosity and altering the column performance. Columns must be returned to the plastic test tubes after use and cleaning.

As the resin floats in water, the resin bed is capped with anion exchange resin. Care must be taken not to disturb the anion resin sufficiently to cause mixing with the underlying Teflon.

Separation of Nd and Sm is performed in very dilute HClx. Under these conditions REE are extremely strongly bound to conventional cation-exchange resins. It is extremely important therefore that no resin particles are carried over from the first column to the reverse-phase columns.

1. Equilibrate column with 15 ml of 0.4M HClx.

2. Dissolve the REE extract with a small quantity (<100 □l) of 0.4M HClx and add to column.

3. Wash into resin with two 200 □l washes.

4. Follow the column log to separate Nd and Sm in 0.4M HClx.

5. Wash column with 50-70 ml each of 6M HClx and H2Oxrx.

Store columns in water in plastic test tubes.

9.7 Pb-Pb columns

There are two sets of eight quartz glass columns. This allows two sets of four columns for each separation.

Take eight 10 ml collection beakers from the storage container, remove cling wrap and place one under each column stand. Pour H2Oxrx off one set of quartz glass columns, remove from washing beaker and place in the individual column stands. (NV: Please wear plastic gloves when doing this. At no stage should the columns be handled without gloves.) Ensure that the frits are in place - use the Teflon coasted tweezers and glass rod to replace any frits that have floated out of the columns. Align the column stands in such a way that the tip of each column is touching the inside or lip of the collection beaker. This will facilitate the flow of reagent through the columns by capillary action. It is advisable to have the beaker spout on the opposite side to the column in order to avoid contamination after discarding waste acid from the collection beaker.

Place 2-3 drops of AG1x8 anion exchange resin from the dripper bottle into each column. It is important to shake the resin well before dripping it into each column so as to ensure an even size distribution of resin particles in each drop. A handy tip is to squeeze the bottle slightly before swirling the resin, so that any fluid left in the "nozzle" after dispensing resin into the column will be drawn back into the bottle when released.

The column chemistry is in no way absolute and the amount of reagents indicated serve only as a guide. A quartz glass column three-quarters full equals approximately 1 ml. The reagents are stored in 125 ml Teflon squirt bottles and are added to the columns directly, being careful not to disturb the resin.

Clean resin with: 2 x 1 ml 0.5M HBrrr

0.4 ml H2Oxrx

2 x 1 ml 0.5M HNO3x

0.4 ml H2Oxrx

The second set of columns are left at this stage until required. Discard the waste acid from the collection beakers at this point.

Precondition the first set of columns with 1 ml 0.5M HBrrr.

Using the micropipette, load sample onto the column. Remember to use a clean pipette tip for each sample. If 100 mg of sample was dissolved, all the supernate from the centrifuge tube may be added to the column. However, if a larger amount of sample was dissolved, then the supernate should be divided proportionately. (For example, for 200 mg of sample, add half the supernate to the column.)

Wash with 2 x 1 ml 0.5M HBrrr.

Collect Pb into cleaned Savillex beakers with 1 ml H2Oxrx. Dry down and cool slightly. Add approximately 0.2 ml 0.5M HBrr, seal and leave to dissolve while preconditioning the second set of columns with 1 ml 0.5M HBrrr. Using the micropipette, add samples to the columns. Proceed as for the first column separation. Collect Pb into a new set of clean Savillex of PTFE beakers. Dry down to approximately half volume. Take four clean planchettes and using the loading pipette, place a small drop of 0.2M H3PO4 into each planchette. Also using the loading pipette, transfer each sample to a planchette and label the planchette beaker with the sample number. Dry down and cool. Seal each beaker with cling wrap. The Pb samples are now ready to be loaded onto outgassed Re filaments for analysis.

9.7.1.1 Cleaning Pb-Pb columns

The resin is discarded and the columns are cleaned between each set of samples. Rinse resin from columns with H2Oxrx, making sure that no resin remains stuck to either the sides of the column or to the frit. Place in column washing beaker and fill with 6M HClx. Heat to 60-80 □C and leave for a minimum of 24 hours. Pour off hot HCl and rinse several times by filling the beaker with H2Oxrx and decanting. Finally, fill the beaker with H2Oxrx, heat to 60-80 □C and leave for a further 24 hours, after which the H2Oxrx may be discarded and the beaker filled with fresh H2Oxrx and stored on a warmer ready for use.

The first tend to go yellow with time. They should therefore be changed periodically. There is a supply of frits kept in a small plastic sample bag. After rinsing out the resin, remove the frit, using a piece of "spaghetti" Teflon, replace with a new frit and proceed with washing procedure described above.

9.7.1.2 Cleaning Pb-Pb waste acid beakers

Waste Collection beakers are rinsed with tap water and then placed in Decon. The cleaning procedure is the same as for the 10 ml glass planchette beakers. Once dry they are covered with cling wrap and stored in an Addis storage container.

9.8 Chromium isotope purification procedure

9.8.1 Method used at SIL (modification of technique at CalTech)

9.8.1.1 Reagents and materials required

- Quartz-glass columns (6-8mm ID) with 0.5 ml of AG1x8 anion resin
- Dilute HCl^x (about 0.2 M) – use the weakest of the HCl solutions used for Sm-Nd Kel-F chemistry so as to avoid making up yet another reagent
- Approximately 6M HCl^x
- Approximately 1M HNO_3^x
- Approximately 7M HNO_3^x (made from 1:1 volume of Milli-Q water and conc. HNO_3)
- Disposable polypropylene beakers
- Ce oxidation solution (made in batches of ~50 ml at a time)

9.8.1.2 Preparation of Ce solution

- Approximately 0.530 g Ceric Ammonium Nitrate dissolved in 25 ml 1M HNO_3

9.8.1.3 Preparation of Ion exchange Resin Columns

- Prior to sample processing, rinse with 5 ml 7M HNO_3^x, followed by 5 ml Milli-Q water and 5 ml 0.2M HCl^x.
- After sample processing, rinse with 10 ml 6M HCl, followed by 10 ml Milli-Q water.
- Store in Milli-Q water.

9.8.1.4 Sample Preparation Procedure

- Take aliquot corresponding to 20 μg Cr (including Cr double spike) for ion exchange chemistry.
- For rock or mineral powders, add required amount of double spike (use a double spike with known ^{50}Cr and ^{54}Cr

- Dissolve overnight in Savillex beaker. If samples contain significant chromitite, it may be necessary to dissolve the sample and spike mixture in a microwave bomb.

- Once one has a dissolved sample (or a sample as water), add 1 ml 1M HNO_3 and 200 µl Ce (IV) solution. Dry to a drop on a hot plate. Add ~5ml 0.2M HCl and transfer to ion exchange column, using a pipettor.

- Allow to run into resin, collect waste reagent in a disposable polypropylene beaker.

- Add ~5ml 0.2M HCl, continuing to collect waste in same beaker.

- Add ~5ml 0.2M HCl, continuing to collect waste in same beaker.

- Flush Cr from resin using ~10ml 7M HNO_3, collected into a second disposable polypropylene beaker.

- Almost dry the Cr solution at ~110 ^{o}C. The high temperature is required to drive off the very viscous nitric acid. It is essential that this solution is not dried completely as it is nigh on impossible to redisolve the Cr. If one must dry the solution, it is necessary to allow the remainder of the solution to dry at less than 20 ^{o}C. Once dried, the Cr should appear black or dark purple. If it is green in colour it will almost certainly not redisolve.

9.8.2Method published by Ellis *et a*l. (2002)

Use a double spike with known ^{50}Cr and ^{54}Cr

9.8.2.1 Ion exchange procedure

- Spike the sample prior to column purification

- Add to AG1x8 resin

- Elute other cations and uncharged species with 0.1 M HCl. Cr^{6+} is retained

- Reduce Cr^{6+} to Cr^{3+} with 0.1N H_2SO_3. This also oxidises SO_3^{-2} to SO_4^{-2}

- Elute Cr^{3+} with 8ml of 0.1 M HCl

- Remove SO_4^{-2} with a second anion exchange column

9.8.2.2 Filament loading

- Mix purified sample (~200ng Cr) with 20µg colloidal silica and 0.6 µl of saturated boric acid

- Load onto single rhenium filament

- Analyse at temperatures from 1150 ^{o}C to 1250 ^{o}C

- Determine ^{50}Cr, ^{52}Cr, ^{53}Cr and ^{54}Cr

External precision quoted by the authors is 0.2 $^{o}/_{oo}$ at 95%

9.8.3Method published by Ball and Bassett(2000)

9.8.3.1 Equipment used

- Miniature ion exchange columns prepared by placing a small plug of quartz wool in a 1 ml piston pipette tip and adding about 0.5ml of AG1x8
- Peristaltic pump provided solutions to the columns at about 0.5 ml per minute, using 0.8mm ID x 4.0 mm OD acid-resistant silicone tubing
- 125 ml Erlenmeyer flask on a hot plate was used to boil samples during the oxidation step

9.8.3.2 Ion exchange procedure

- Condition anion exchange resin immediately before use with 2ml each of 6M, 4M, 2M and 1M HNO_3 followed by 15ml H_2O
- Condition cation exchange resin with 5ml of 5M HNO_3 followed by 15ml H_2O
- Spike sample with double spike (^{50}Cr and ^{54}Cr)
- Add sample to AG1x8 resin
- Reductively elute Cr^{6+} with 5ml 2M HNO_3 followed by 5ml H_2O
- Dilute to 150-175 ml with H_2O
- Add sample to AG50Wx8 resin. Discard effluent.
- Rinse with 5ml H_2O. Discard effluent.
- Elute retained Cr with 5ml 5M HNO_3
- Analyse 1/50th of this eluate to determine total Cr concentration
- Pipette sufficient of the eluate to contain about 665 ng Cr into 7ml savillex PFA vial.
- Place on hotplate at 25% setting and cover with vented lid under heat lamp
- Evaporate to dryness
- To destroy residue from the resin, add 75µl HCl and 25µl HNO_3 and evaporate to dryness

- Add 100µl concentrated HNO_3 to convert Cr to nitrate form and evaporate to dryness

9.8.3.3 Filament loading

- When ready to analyse, add 2 µl 0.1M HNO_3, 2 µl well-shaken silica gel suspension and 1 µl 0.25 N H_3BO_3
- Load on filament and evaporate to dryness at low filament current
- Increase filament current for about 5s to drive off traces of residual water

9.8.4Method published by Götz and Heumann(2000)

From complex matrices like sediments, soil and sludge, or also from plants with higher copper concentration (>10 µg/g) , chrome can not, or only non-reproducibly, be separated by electrolysis.

From these matrices a chromatographic method using anion exchange (AG1-x8, 200-400 mesh, Bio-Rad) is used. After samples dissolution, the sample is twice digested with 2ml conc HCl to get rid of the left over HNO_3. After, 2ml HCl and 6ml H_2O is added. The solution is pumped using a peristaltic pump into a glass column filled with the anion exchanger (quartz glass; 5 mm ID; 10 cm filling height). Cr^{3+} will, under these circumstances, not be bound onto the exchange resin and thus will be obtained in the eluant of 3-5 ml. Zn^{2+}, Cd2+, Pb^{2+} and Fe^{2+} will, however, be bound and can later be separated.

For matrices with higher iron concentration (soil, sediments) it is recommended to separate the iron together with chrome in a first column so as to avoid overuse of the capacity of the exchanger. Here the added solution is only is needed to have a 0.5 – 1.0 mol/l HCl concentration. In this case, the iron will be separated from the chrome in the following second column separation. For this, Cr3+ of the first column separation will be oxidised in a quartz flask to Cr6+ in boiling heat after filling it up with H2O to approximately 100 ml with 1 ml 1 mol/l $(NH_4)_2S_2O_8$ solution.

The separation of Cr^{6+} will take place in above described separation column. For this, the column will first be regenerated with 20 ml of 2 mol/l HNO_3 and 60 ml 0.5 mol/l HCl and then neutralised with 30 ml H_2O. Then the Cr^{6+} solution will be added, resulting in chromate being strongly bound by the anion exchanger. Firstly, using 15 ml of 0.04 mol/l HCl, iron will be eluted. Then chrome will be separated as a sharp band (about 3 ml) using 2 mol/l HNO_3. Chromate will thus be reduced to Cr^{3+} after addition of HNO_3 and no longer be bound.

Chrome can also be concentrated using above described chromatographic method out of several litres of a water sample. To water sample, spiked with 1 ml conc HCl, 1 ml of a 1 mol/l $(NH_4)_2S_2O_8$ solution is added and in a flask heated for about 15 minutes at boiling point. After cooling, the solution is pumped using a peristaltic pump onto the above described anion exchange column, there concentrated as Cr^{6+} and then eluted as Cr^{3+}.

10 Ion exchange resins

10.1 Calculation of "q" or loading parameter for columns

Following Strelow (1960):

$$q = \frac{\text{total amount of cations in the exchange system}}{\text{total resin capacity}}$$

For small (2.5 g) columns, resin capacity = 2.5 x 5 = 12.5 meq

		0.1 g	0.2 g	0.5 g
i	Average granite	0.0506	0.1012	0.2530
ii	Average tonalite	0.0670	0.1340	0.3350
iii	Average dolerite	0.0833	0.1665	0.4163
iv	Average nepheline syenite	0.0770	0.1539	0.3847

Assuming one has two columns with 0.25 g and 0.50 g resin

Use 0.1g sample on the smaller column

0.2g sample on the larger column

if one wants to keep constant loading factor "q"

10.2 Calculation of meq/g for average dolerite

		Test sol meq/0.25 ml
Al	0.90	0.9
Fe	0.33	0.045
Ca	0.33	0.035
K	0.022	0.0028

	meq/0.1 g rock	test solution	
	Le Maitre average	meq/0.25 ml	mg/0.25 ml
Al	0.90	0.9	809
Fe	0.33	0.045	895
Ca	0.33	0.035	715
K	0.022	0.0028	104
Sr	200 ppm	20 µg	22 µg
Rb	100	10 µg	15.48 µg

For testing of the smaller (2.5 g) columns,

Draw 0.25 ml aliquot

Dry down

Take up in 1 ml of 2.5 M HCl

Centrifuge

Load supernate

Resin	Capacity (1 ml)	Capacity (5 ml)	Capacity (10 ml)
AG1x4	1.2	6.0	12
AG1x8	1.4	7.0	14
AG50Wx8	1.7	8.5	17
AG50Wx12	2.3	11.5	23

Rock maximum = 2 meq/g (excluding SiO_2

Therefore 0.5 g sample = 1 meq

Hence, for AG1x8, q = 0.7 (for 1 ml resin)

q = 0.35 (for 2 ml resin)

10.3 Cation resins

10.3.1 AG50Wx8 and AG50Wx12

AG50Wx4 HBr

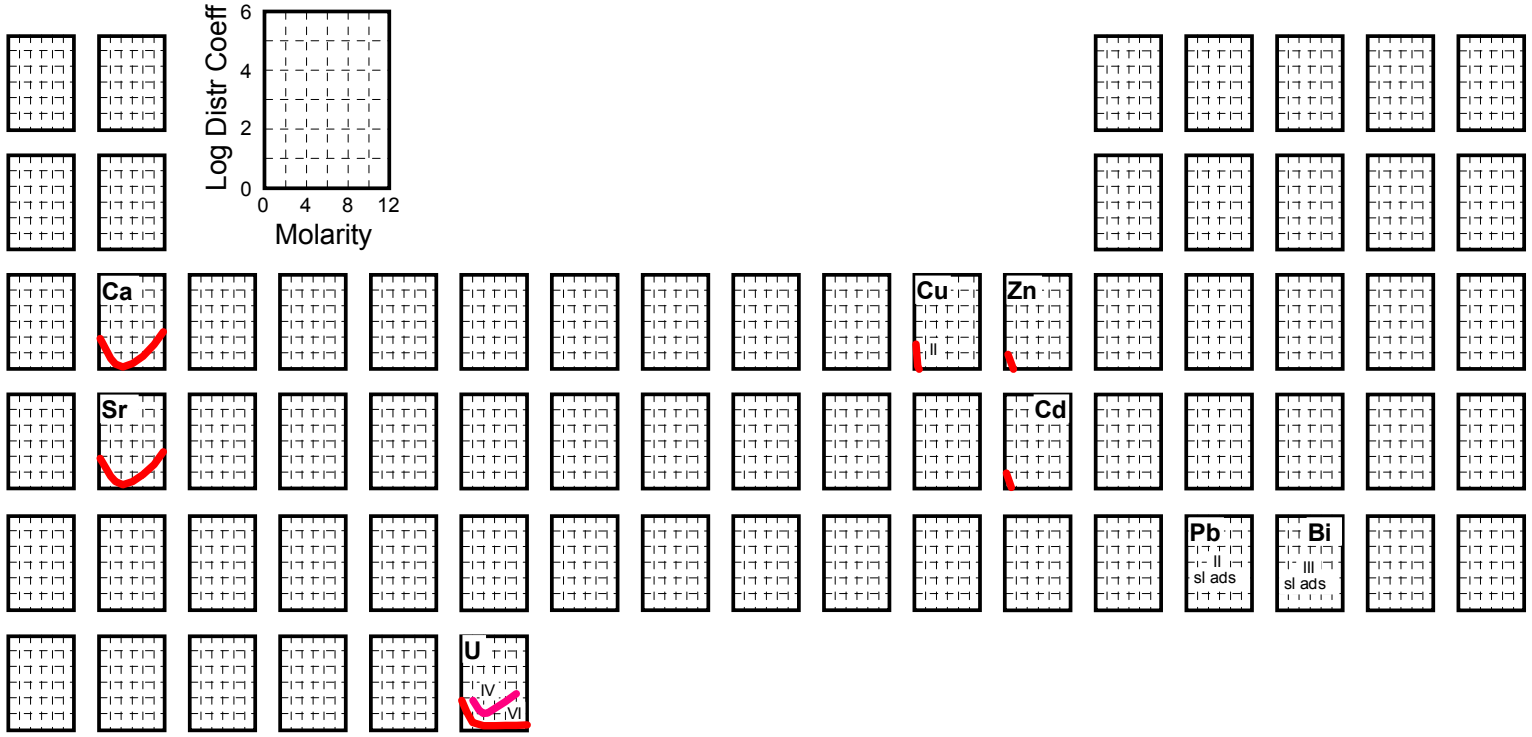


Figure 4. Variation of distribution coefficient for different elements in HBr on AG50Wx4 cation resin.

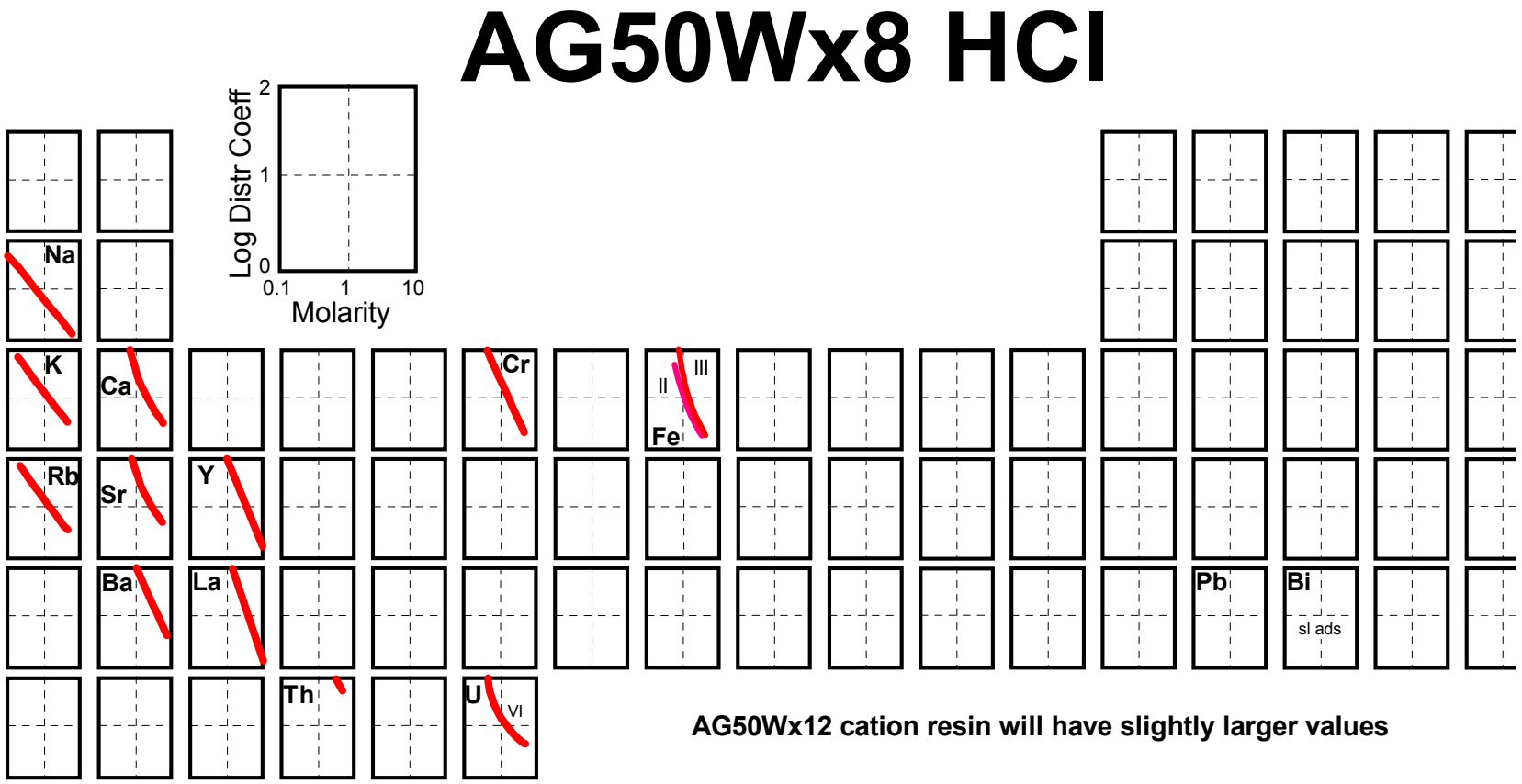


Figure 5. Variation of distribution coefficient for different elements in HCl on AG50Wx8 cation resin.

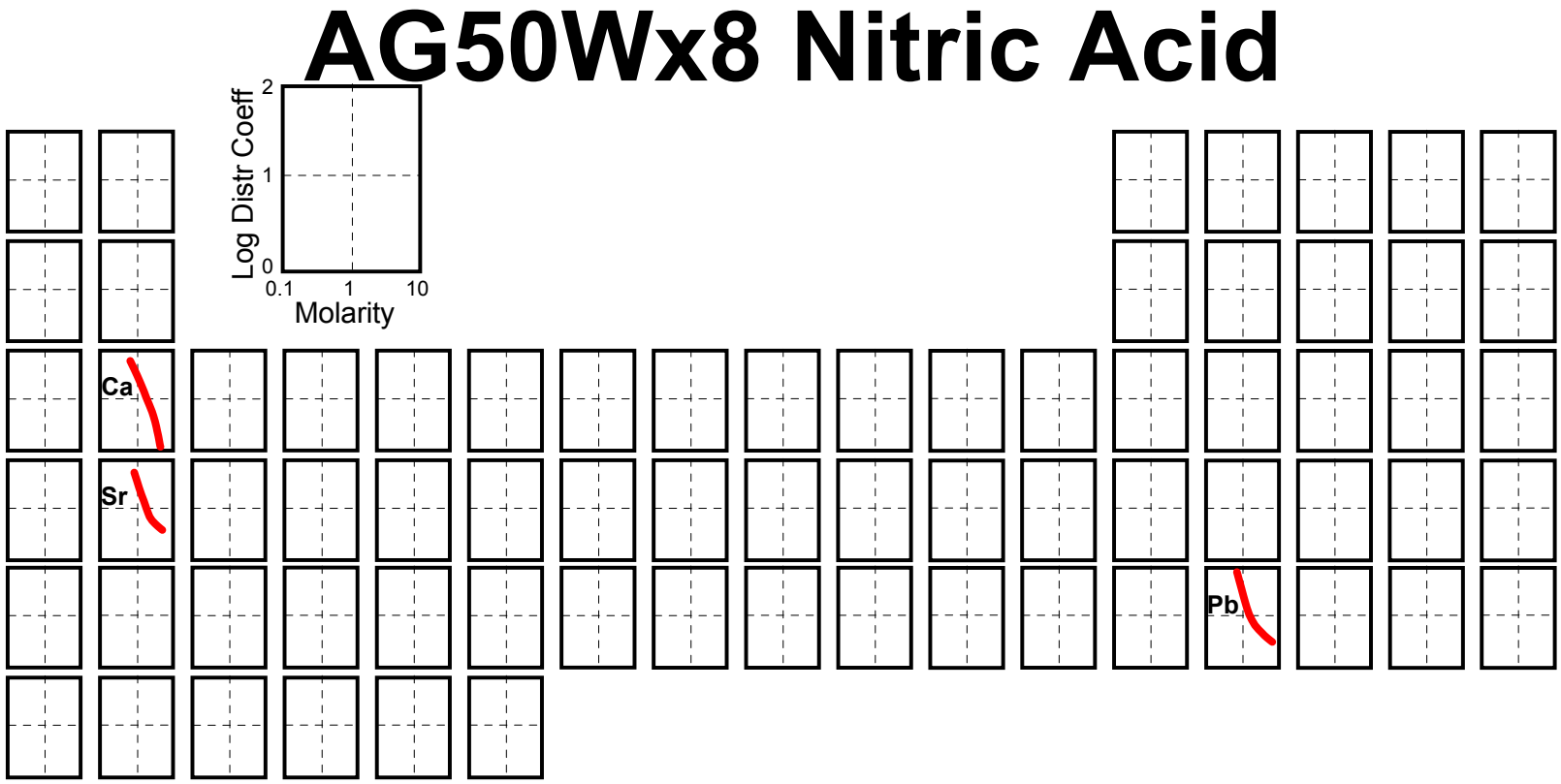


Figure 6. Variation of distribution coefficient for different elements in HNO_3 on AG50Wx8 cation resin.

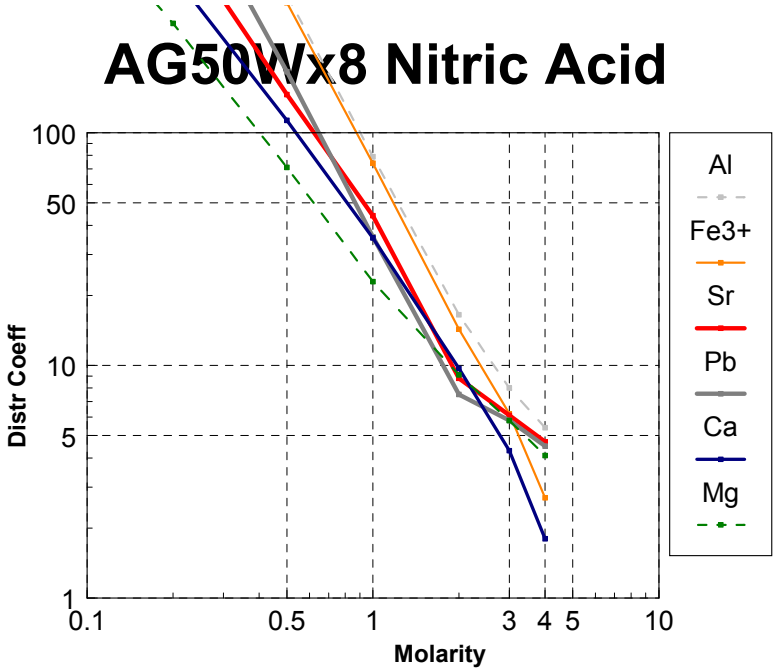


Figure 7. Variation of distribution coefficient for different elements in HNO_3 on AG50Wx8 cation resin.

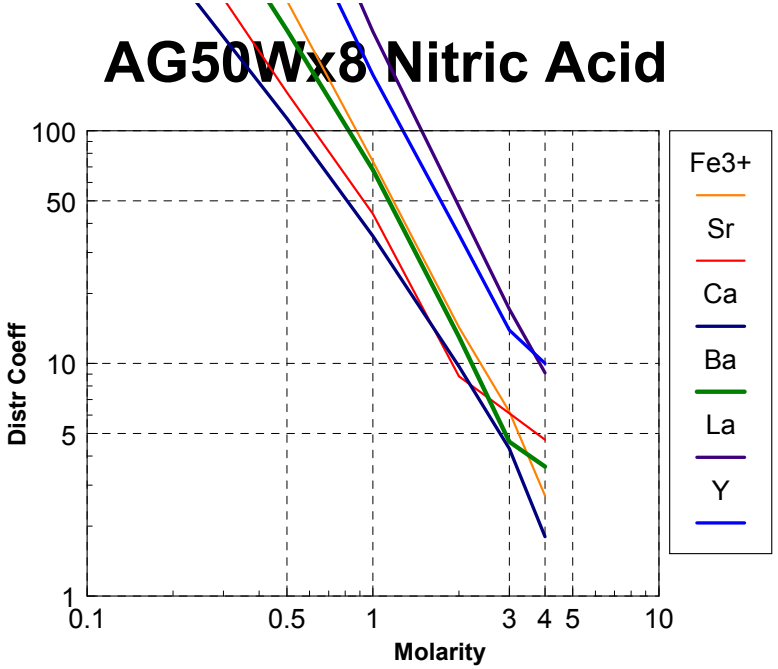


Figure 8. Variation of distribution coefficient for different elements in HNO_3 on AG50Wx8 cation resin.

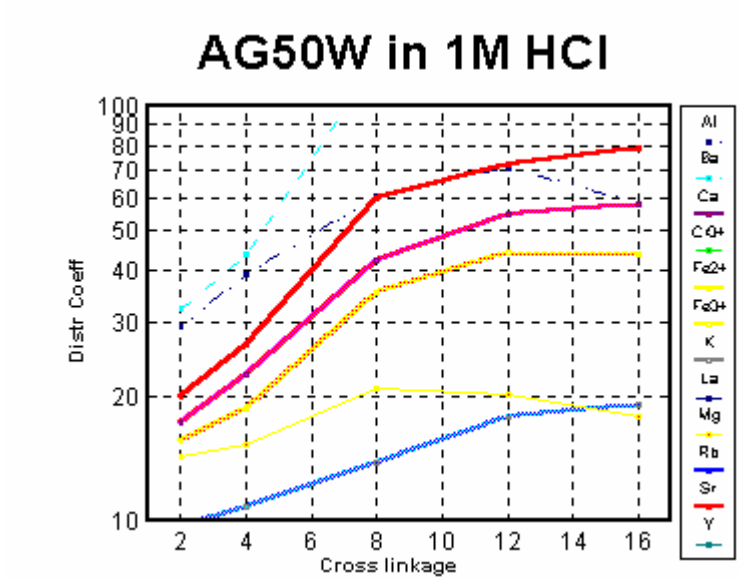


Figure 9. Variation of distribution coefficient for different elements in HCl with different cross-linkages of AG50Wx8 cation resin.

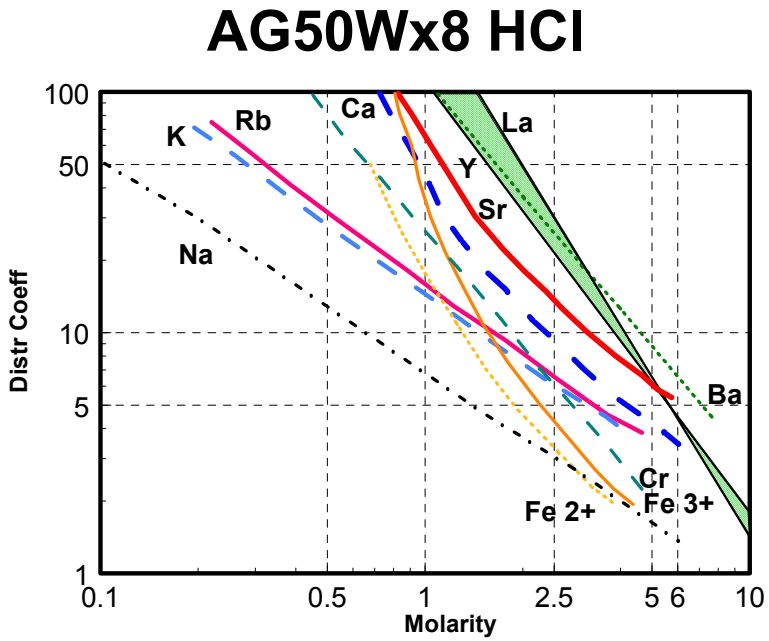


Figure 10. Variation of distribution coefficient for different elements in HCl on AG50Wx8 cation resin.

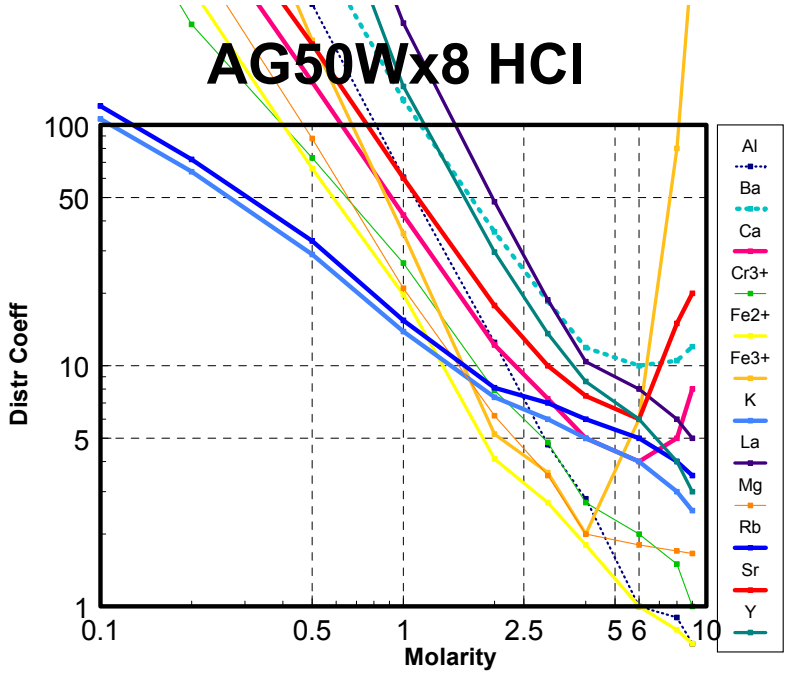


Figure 11. Variation of distribution coefficient for different elements in HCl on AG50Wx8 cation resin.

10.3.2 AGMP-50

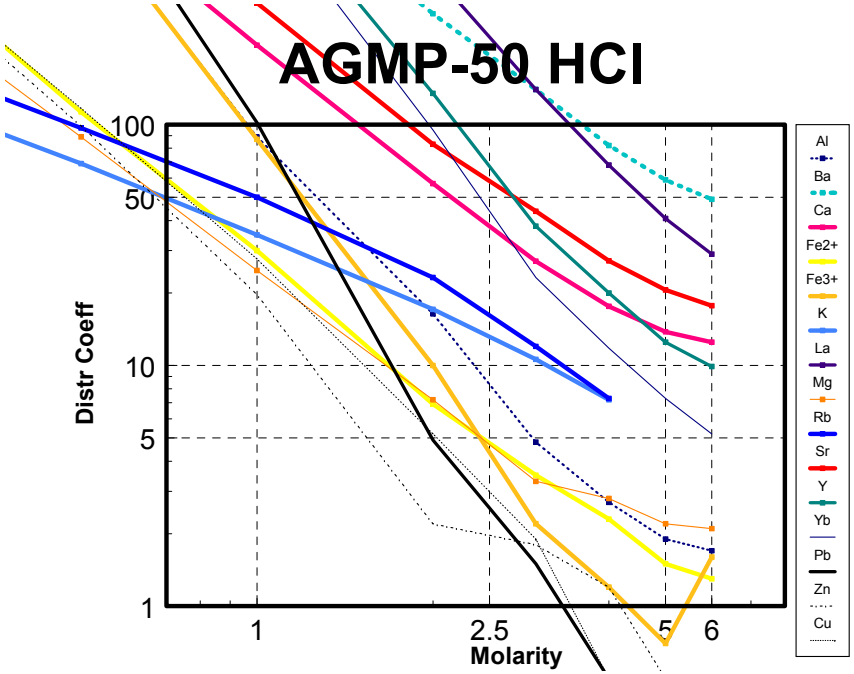


Figure 12. Variation of distribution coefficient for different elements in HCl on AGMP-50 cation resin.

10.4 Anion resins

10.4.1 AG1x8

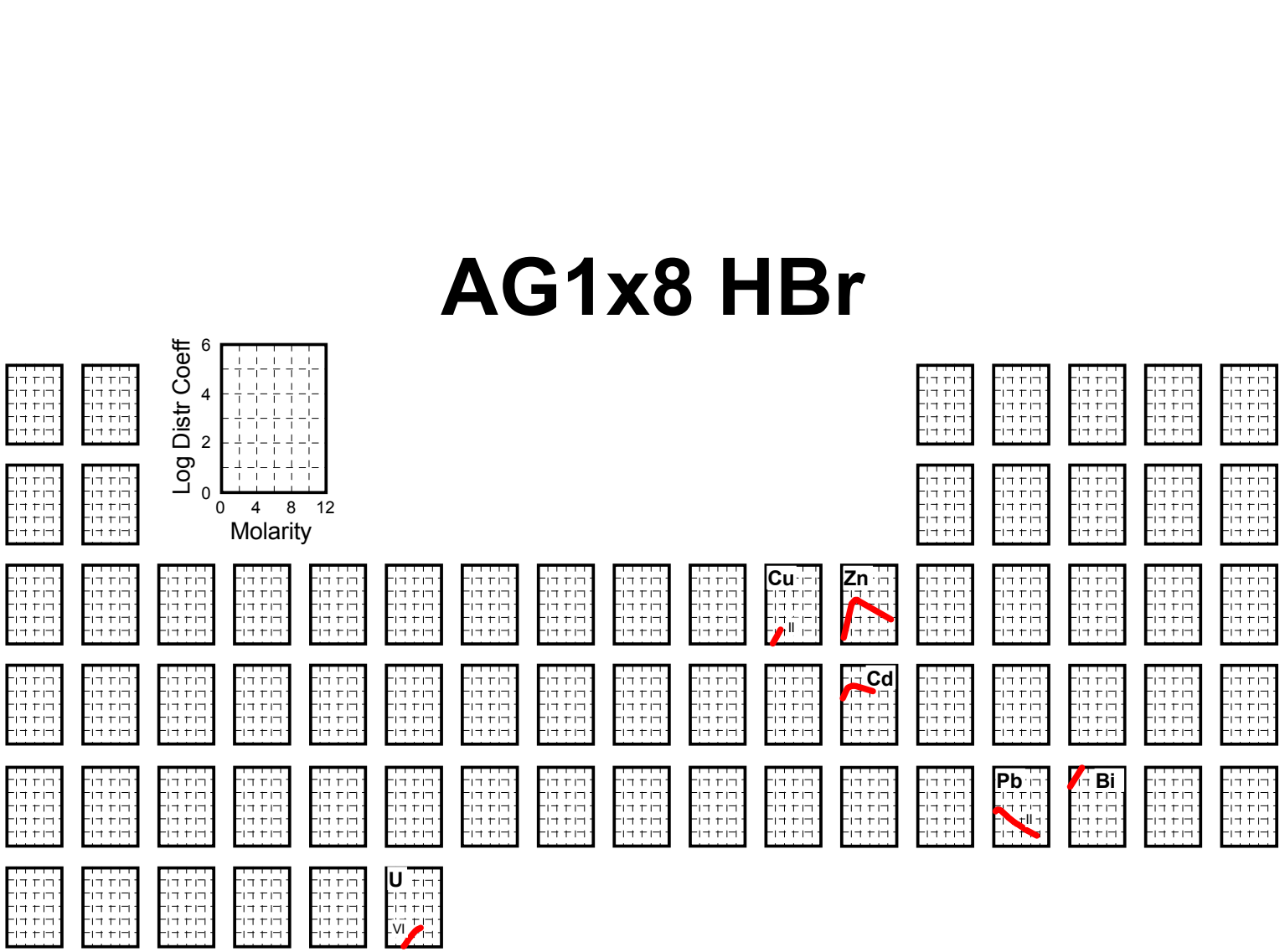


Figure 13. Variation of distribution coefficient for different elements in HBr on AG1x8 anion resin.

AG1x8 HCl

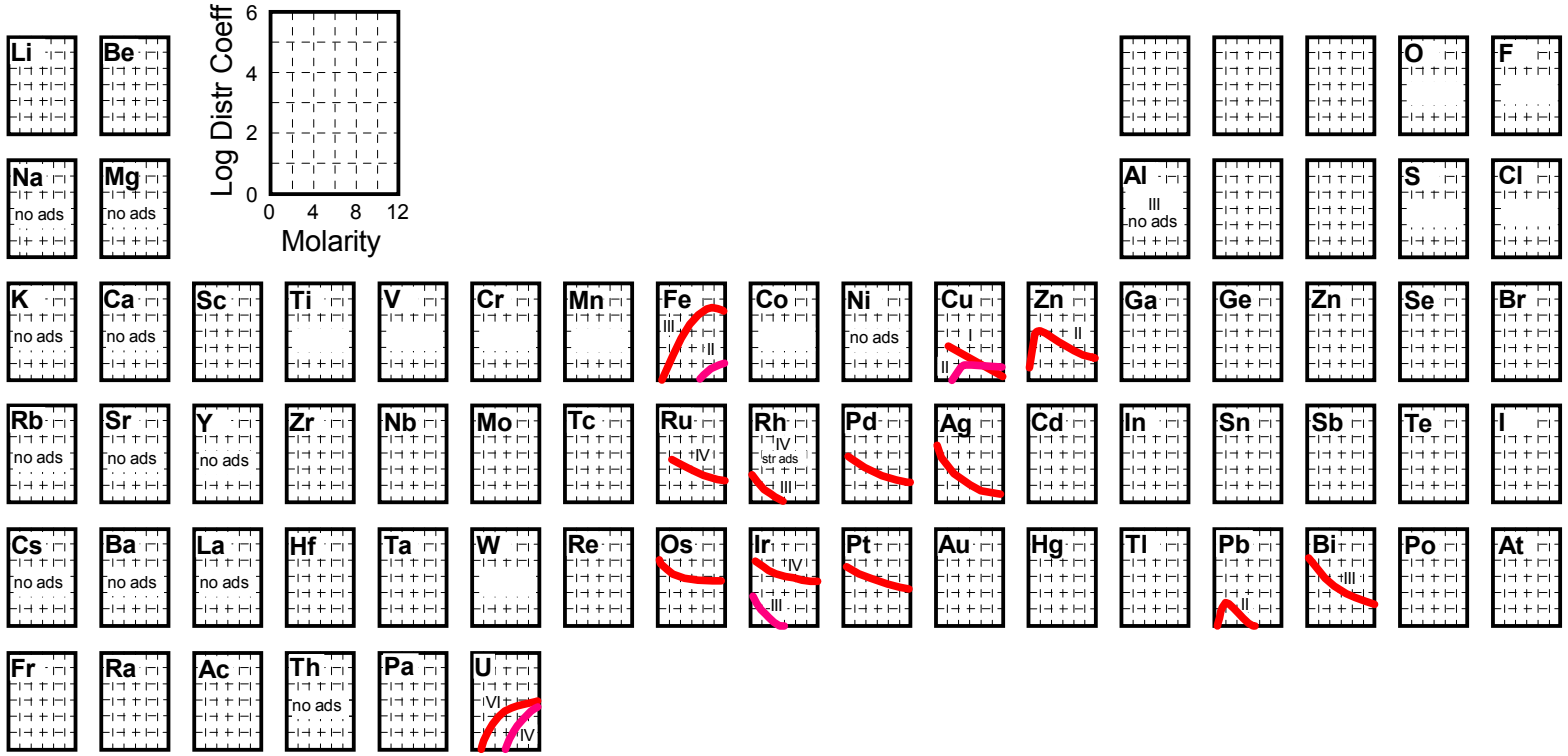


Figure 14. Variation of distribution coefficient for different elements in HCl on AG1x8 anion resin.

AG1x8 Nitric Acid

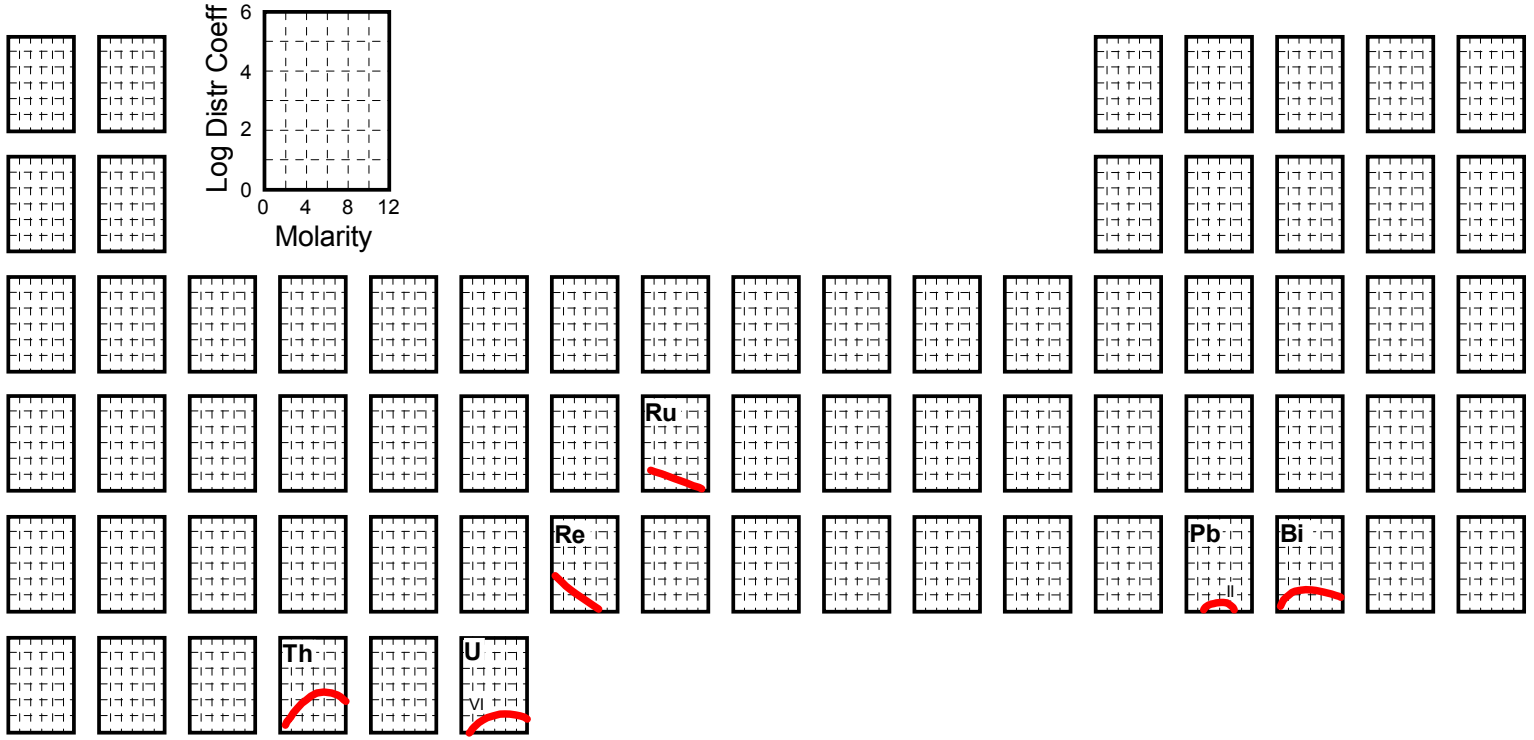


Figure 15. Variation of distribution coefficient for different elements in HNO_3 on AG1x8 anion resin.

10.5 Kel-F

10.6 Eichrom element-specific resins

10.6.1 Sr spec

10.6.2 TRU spec

10.6.3 LN spec

11 Calibration of ion exchange columns

11.1 Cation resins

11.1.1 AG50Wx8 and AG50Wx12

11.2 Anion resins

11.2.1 AG1x8

11.3 Kel-F

11.3.1 Etiochrome Black-T (EBT)

11.3.2 Chlorophosphanazo III (CPA-III)

11.3.2.1 Abstract

Calibration of the ion exchange chromatography columns used in the separation of REE for isotope analysis is commonly performed by titration with Eriochrome Black-T. This indicator requires careful adjustment of the pH prior to use and the indicator solutions have limited shelf life. In this communication we describe an alternative indicator, chloro-phosphonazo-III, which operates effectively at the acid molarities commonly used on Kel-F ion exchange columns and has indefinite shelf life.

11.3.2.2 Introduction

Chromatographic extraction of individual rare earth elements (REE) from geological materials is required for isotopic analysis by thermal ionisation mass spectrometry (TIMS). A commonly used separation technique for the purification of Nd and Sm utilises reverse phase liquid chromatography principles with the exchange medium (bis-2-ethyl-hexyl-hydrogen phosphate: "HDEHP") supported on Teflon powder, the so-called "Kel-F" technique (Richard *et al.*, 1976) which is now available commercially as LN resin. Maintenance of these chromatographic columns involves regular and precise calibration by adding a solution containing REE and monitoring aliquots of

the eluant for the REE of interest. Most laboratories have used Eriochrome Black-T (EBT) as an indicator for this purpose (Zindler, 1980; Shirey *et al.*, 1987).

This note discusses the advantages of an alternative reagent, Chlorophosphonazo-III, as an indicator for routine calibration of Kel-F ion exchange columns.

11.3.2.3 Chlorophosphonazo-III

Chlorophosphonazo-III (CPA-III), the chemical 2,7-bis(4-chloro-2-phosphono-benze)-1,8- dihidroxynaphthalene-3,6-disulphonic acid), is a sensitive indicator used in spectrophoto-metric analysis of uranium (Strelow and Van der Walt, 1979; Strelow and Van der Walt, 1981) and other elements. Strelow and Van der Walt (1979) commented that elements such as Zr, Hf, Th, Sc, Y and REE also induce colour changes in CPA-III which results in strong interference on the photometric signal for U.

In view of this response, the use of CPA-III as an indicator for the REE was investigated.

Advantages of CPA-III over EBT

EBT testing solutions are prepared by mixing EBT powder with methanol and NH_4OH. Solutions more than a few days old do not provide accurate colour changes and so fresh batches of indicator need to be prepared for each calibration. Prior to testing with EBT, aliquots of eluant are first buffered to a pH value of 9-10 with ammonia otherwise the action of the indicator (colour change from blue to red) is suppressed.

By contrast, CPA-III indicator solutions are prepared in dilute HCl and have an almost indefinite shelf life. The response of CPA-III to cations is greatest in solutions with a pH close to 1, roughly equivalent to 0.1M HCl solution. Nd is usually eluted from Kel-F columns with HCl of low molarity - our laboratory uses 0.2M HCl. As a consequence, no buffering or pre-preparation of any kind is required - the presence of REE is sensitively detected by simply adding a few drops of CPA-III solution directly to the eluted aliquot.

CPA-III has been used successfully in various laboratories since 1985 for routine calibration of cation and Kel-F ion exchange columns. During this period, CPA-III solutions have been shown to have a shelf life of at least several years.

11.3.2.4 CPA-III : method and sensitivity

A working solution of CPA-III is made up as a ~ 0.025 % concentration of CPA-III powder (Fluka Catalogue #26049) dissolved in dilute HCl - we use 0.2M HCl. The required element, or group of elements, is added to the ion exchange column and eluted with appropriate eluant(s). One ml aliquots are collected off the Kel-F columns, approximately 100 μl of CPA-III solution (equivalent to 2-3 drops) is added to each aliquot and the colour noted against a white background. A colour change from purple to light green indicates the presence of dissolved cations. CPA-III is ineffective at high acid molarities (see below) , so calibration of cation exchange columns (AG50W-X8 in 2.5M or 6M HCl) for the bulk REE requires that the aliquots (2-5 ml) are first dried. Testing with CPA-III is then performed after the addition of ca. 1ml of 0.2M HCl.

The sensitivity of CPA-III for the rare earth elements and the influence of HCl acid molarity on colour was ascertained in a series of tests reported below.

Nd was used to test the sensitivity of CPA-III to REE concentration. Test solutions, ranging from ~ 165 ppm to <0.1 ppm, were prepared in 0.2M HCl and ~ 100 μl of 0.025% CPA-III solution added to each. The colour

variations (including their Pantone colour codes) obtained in these tests are provided in Table 1. These tests indicate that Nd is easily detected at concentrations down to 2-3 ppm, below which no colour variation is evident.

11.3.2.5 Effect of Acid Molarity on the Colour Change

Strelow and Van der Walt (1979; 1981) noted that the effectiveness of CPA-III is dependent on the acid molarity of the solution in which the cations are dissolved. A series of tests were therefore performed to establish the response of CPA-III in HCl molarities of 0.1M to 6M, i.e. molarities ranging from those typically applied with Kel-F columns (Richard *et al.*, 1976) and LN columns to those used with AG50W cation exchange columns.

Three sets of twelve solutions were prepared, as described in Table 2. The first set contained only 2 ml HCl and 100 µl of 0.025% CPA-III solution. Set 2 contained HCl, CPA-III and 20 ppm of Nd, whilst Set 3 had Ba in place of Nd. pH was measured for each of the acid concentrations in Set 1 and are given in Table 2. Table 2 also describes the colour of the indicator solution obtained for the various acid molarities. The CPA-III solution retains its purple colour in the absence of Nd and Ba at all molarities up to 3M HCl, but changes to a green colour at higher acid concentrations.

The CPA-III solution displays a characteristic light-green colour in the presence of Nd at molarities up to 0.75M HCl beyond which the indicator action is inhibited and the CPA-III remains purple. A light green colour is again evident at 6M HCl. In the presence of Ba, CPA-III solution displays a light blue colour at low molarities whereas a purple-blue colour is apparent above 0.5M HCl.

It is obviously also possible to use CPA-III for the calibration of bulk rare earth elements from columns requiring acid more concentrated than the 0.5M limit determined above but, in these cases an additional step in the procedure is required. It becomes necessary to dry the more concentrated solution and take up the product in suitably dilute HCl (say 0.4M) before testing the colour. The CPA-III provides significant advantages as regards time relative to alternative techniques for calibrating such cation columns e.g. atomic absorption analysis of the solutions.

11.3.2.6 Conclusions

Chlorophosphonazo-III is a reasonable indicator of the presence of Ba and a good indicator for the rare earth elements at concentrations above 2-3 ppm in HCl solutions of 0.5M or less. The long shelf life and ease of use of CPA-III makes it a better choice for calibration of Kel-F type (Richard *et al.*, 1976) and LN resin Sm-Nd separation columns than Eriochrome Black-T. The indicator may also be used with columns utilising more concentrated acid, provided that the aliquot collected is dried and the concentrate redissolved in suitably dilute HCl.

11.3.2.7 Acknowledgments

Dr Strelow is thanked for suggesting the use of CPA-III as an easy calibration method for REE separation columns.

Table 1. Colour of CPA-III solution in the presence of Nd at various concentrations.

Nd concentration (ppm)	Colour	Pantone colour code
164.70	Light green	326 C
82.30	"	"
41.20	"	"
20.60	"	"
10.30	"	"
5.20	"	"
2.60	"	"
1.30	Purple-blue	272 C
0.60	Purple	528 C
0.30	"	"
0.20	"	"
0.08	"	"
0.00	"	"

Table 2. Colour variation of 100 μl CPA-III indicator solution with acide molarity and nature and concentration of dissolved cation.

Set 1: no dissolved cation;

Set 2: 20 ppm Nd;

Set 3: 20 ppm Ba

Beaker# :	1	2	3	4	5	6	7	8	9	10	11	12
M HCl	0.10	0.20	0.40	0.50	0.75	1.00	1.25	1.50	2.00	2.50	3.00	6.00
pH	1.13	0.87	0.62	0.53	0.35	0.24	0.15	0.06	<0.05	<0.05	<0.05	<0.05
Set 1:												
Colour	P	P	P	P	P	P	P	P	P	P	P	PB
Set 2:												
Colour	LG	LG	LG	LG	LG	PB	PB	PB	PB	PB	PB	LG
Set 3:												
Colour	LB	LB	LB	LB	PB	PB	PB	PB	PB	PB	PB	PB

Explanation of colours:

P = Purple : Pantone colour code 528C

PB = Purple-blue : Pantone colour code 272C

LG = Light green : Pantone colour code 324C

LB = Light blue :Pantone colour code 312C

11.4 Eichrom element-specific resins

11.4.1 Sr spec

11.4.2 TRU spec

11.4.3 LN spec

Volume

5

Sampling

12 Rock samples

13 Water samples

13.1 Introduction

The purpose of this manual is to provide ground water sampling techniques that will ensure that all ground water data collected is representative of actual *in situ* ground water quality. Users following these techniques should reduce sampling error to a minimum and ensure that the data is reliable.

A PROPERLY COLLECTED WATER SAMPLE IS CHEAPER THAN HAVING TO RETURN TO THE SITE TO RE-COLLECT A SAMPLE WHICH WAS POORLY COLLECTED THE FIRST TIME

One of the most important steps is to liaise with the analytical laboratory. Discuss the laboratory's requirements for testing, such as sample quantities. At least one full 250 ml bottle will be needed for Sr isotope analysis and one full 400 ml bottle for Pb isotope analysis.

13.2 Trace and Heavy Metals

Generally the trace and heavy metals are relatively immobile under normal ground water flow conditions. When low pH and/or Eh occurs, as is typical at many pollution sites, the metal contents may become a factor. The reason for this is that, under these conditions, the metals may be in the soluble phase and become mobile. When the ground water is brought to the surface, CO_2 degassing and exposure to the atmosphere occurs, pH rises, Eh

tends towards oxidising conditions and then the valence state of some of these metals can change, consequently their **solubility** changes and they will precipitate or plate out onto the sample bottle.

In addition, when iron or manganese precipitate, they are strong **scavengers** (adsorption) and this will change the metal concentration. It is therefore very important to collect a **filtered** sample for metal analysis. This filtered water should immediately be acidified to a pH < 2 to prevent the metals from precipitating and being adsorbed onto the walls of the container. The filtration should take place as rapidly as possible after the ground water has been brought to the surface and with minimum exposure to the atmosphere.

When a water sample is not filtered, suspended solids are collected as well. If this water sample is then acidified and analysed for metals, the results merely represent the muddiness of the water sample as metals will be leached by the acid from the clay particles and suspended solids.

If a laboratory receives an unfiltered water sample and is requested to analyse selected metals, the standard practice is to let the sample stand for a few days (or centrifuge the sample, decant the liquid, filter and analyse. This is meaningless for ground water interpretation purposes, as by this stage most, if not all, metals will have either precipitated out, plated out or have been scavenged by iron and manganese.

Thus, if trace and heavy metals are to be analysed, it is most important to filter the sample and to state so on the sample bottle label. It is even better to liaise with the analytical laboratory before going into the field. Ensure that they know what you are doing and what you expect from them.

13.3 Sample Bottles

Glass or plastic sample bottles can be used. **Plastic** is preferable as the glass can break more easily. Either polyethylene or polyvinylchloride (PVC) plastic bottles can be used. Polyethylene is preferred as less adsorption occurs than on PVC. The background radio-activity for polyethylene bottles is also lower than that of glass containers. **Glass** bottles must be of borosilicate glass and preferably a dark colour to reduce photo-degradation of the sample and growth of biological matter but note that borosilicate glass can not be used when collecting water for Pb isotope analysis.

Make sure the sample bottle used is **clean**. Bottles should be rinsed with 6 M HCl to make sure that all leachable material has been removed. Rinsing afterwards with XRX water will remove any remaining material and acid. This should be done prior to leaving for the sample site. Be very careful not to touch the inside of the bottle or the cap. Bottles to be used for the collection of water for trace or heavy metal analysis should be **acidified**. One may use either HCl or HNO_3 for this purpose but HNO_3 is preferred because the sample can then also be analysed by ICP-MS without introducing interference from chloride compound peaks. In order to achieve a pH of ~2 in the final sample, assuming typical ground water conditions, one should add the following amounts of 3M HNO_3[x] :

250 ml bottle - 2ml of 3M HNO_3

500 ml bottle - 4ml of 3M HNO_3

Marking the sample bottle correctly is very important, as a sample without identification is worthless. The best method is to use a waterproof felt-tip pen and one can cover the writing with clear adhesive tape as a protective measure. Included on the bottle label should be the following:

Sample identification

Sample site

Date of sampling.

Marking a bottle in duplicate can also do no harm.

13.4 Sampling in the Field

The sampler will be equipped with two clean 250 ml polyethylene bottles per sample, a 50 ml syringe with one Swinnex filter holder and enough 0.45 μm filter paper.

One plastic bottle will contain enough acid to adjust the pH of the filtered water to ~2, while the other will be used to collect the sample from the site. The latter bottle, together with the syringe and filter holder, must be rinsed with sample water at least twice - this includes the cap of the bottle too. As soon as the sample is collected, it should be filtered into the bottle containing the acid:

Unscrew filter holder and put filter paper in. Close very tightly - use plastic tightening wrenches.

With the filter holder connected to the syringe and the plunger removed, water can easily be poured from the plastic bottle into the syringe. The filter and holder keeps it from pouring out at the bottom. Carefully put the plunger back and filter the sample into the correct bottle. After filtering, disconnect the filter holder, take out the plunger and put the filter holder back. Fill the syringe again and repeat until the bottle is filled.

IMPORTANT - USE NEW FILTER PAPER FOR EACH SAMPLE

Close bottles tightly and keep in a cool place out of the sun.

13.5 Sampling of Specific Sites

13.5.1.1 Boreholes

A borehole must be **purged** in order to remove stagnant water from the borehole in order to obtain ground water that is representative of the *in situ* ground water. Stagnation modifies ground water chemistry to the extent that samples may be totally unrepresentative of the formation water.

Purging a borehole in practice, is the removal of sufficient water so that the field chemistry, such as pH, is stable. For most cases this requires removal of three times the volume of the standing water in the borehole.

The field procedure for purging includes measuring the water level and the borehole depth. The hight of the water column = (borehole depth - depth to water level). The standing volume of water in litres can be calculated by substituting in the following formula:

Volume of standing water = π x (radius of borehole)^2 x (height of water column) x 1 000

in metres in metres

The borehole should thus be pumped until three times the volume of water calculated has been removed. Dispose of the purged water safely so that cross-contamination will not occur.

Some boreholes to be sampled are low-yielding and when purging they go dry. Leave the borehole to recover for a few hours before taking a sample which should be representative of the borehole.

If the borehole becomes turbid or is silty then the borehole should be re-developed before the next sampling run. Purging may be too rapid, so reduce the pumping rate to check whether turbidity reduces.

13.5.1.2 Springs

The sampling of a spring is a straightforward procedure in that there is no need to purge. Be very careful not to allow cross-contamination. The best way to reduce cross-contamination is to use your borehole sampling pump and put it in the flowing water as close to the spring outlet as possible. Rinse sample bottles (without acid) and caps in the spring water at a point as close as possible to the source, then collect the source.

13.5.1.3 Seeps

Dig out seeps, let them flow until the water runs clear, sample as a spring. If necessary, install a well screen in the middle of the seep, develop it, and return the following day when the water has cleared. If possible, a seep should be sampled after a wet period.

13.5.1.4 Rivers

Sampling should take place at a point where the river is flowing at a fairly good rate and where the water is not turbid. If, for some reason, a sample is taken at a stagnant point, make sure not to disturb the underlying mud or sand. Get a "clean" sample!

13.5.1.5 Pits

Again, the main concern is to get a "clean" sample with as little turbid water as possible.

Chapter 5

Radiogenic isotope mass spectrometry

14 Filament loading procedures

One must be particularly careful not to contaminate the loading solutions as this will not be easily detected and could affect other users for many months. Do not touch the solution dripper tips. Squeeze the dripper bottles slightly before expelling reagent -they will suck back any reagent remaining in the dripper spout when you release the bottle. Expel a few drops of reagent onto a small piece of clean parafilm and take reagent from the parafilm for each bead. Do not take direct from the dripper bottle.

14.1 Strontium and Samarium

Use outgassed single Ta filaments.

1. Using gloves and tweezers, transfer the filament from the box to the loading-bay.

2. Rinse a pipette tip with 1M $HNO_3^x/H_3PO_4^{sp}$.

3. Take up a small amount of 1M $HNO_3^x/H_3PO_4^{sp}$ in the pipette and put a drop into the sample beaker. Using the pipette tip, roll drop around the bottom of the beaker so as to dissolve the sample. (Try not to pick up too much resin in the drop - this will lead to instability of the Sr beam in the mass spectrometer.)

4. Take up sample from the beaker with the pipette and load centrally on to filament.

5. Expel remaining sample solution back into the beaker.

6. Dry down at 1A.

7. When dry, turn of lamp, increase current gradually until phosphoric acid on the filament starts to fume. After fuming is complete turn up ammeter again until filament just glows red. Hold for 1-2 seconds and then turn down to zero.

8. Return filament to box using gloves and tweezers as necessary.

14.2 Rubidium

Use outgassed double Ta filaments.

1. Use metal tweezers to bend out side filament so that it is ready for loading.

2. Rinse a pipette tip with H_2O, and then take up a small amount of H_2O and put a drop into the beaker. Roll drop around the beaker with the pipette tip, take up sample and load centrally on to side filament. Be careful not to load any sample onto the centre filament as this will result in extreme fractionation during the mass spectrometer run.

3. Expel remaining sample solution back into beaker.

4. Dry down at 1A under lamp.

5. When dry, raise current to 1.5A and hold for 1-2 seconds; then increase again to 2A for another 1-2 seconds, and turn down to zero.

6. Knock off any calcium cake which might have formed on the side filament. Do not worry, this cake does not contain any Rb.

7. Use metal tweezers to return the side filament to its correct configuration.

14.3 Lead

Use outgassed single Re filaments.

1. Using gloves and tweezers, transfer the filament from the box to the loading-bay.

2. Take up a small amount of silica gel into the pipette and load a drop centrally on to filament.

3. Increase the current to O.8A and evaporate to a thin film. **Do not allow the silica gel to dry.**

4. Take up small amount of 1M $HNO_3^x/H_3PO_4^{sp}$ into the pipette and put a drop into beaker. Using the pipette tip, roll drop around the bottom of the beaker so as to dissolve the sample. (Try not to pick up resin in the drop - this will lead to instability of the Pb beam in the mass spectrometer.)

5. Take up sample from the beaker with the pipette tip and load about 500 ng of Pb onto the silica gel.

6. Expel remaining sample solution back into planchette.

7. Raise current to 1A, switch on lamp and dry down to a thin film.

8. At this stage one may repeat steps 2-5. Remember to use a NEW pipette tip for this otherwise the reagents will be contaminated by your sample.

9. When dry, turn off lamp and increase current gradually until phosphoric on filament just starts to fume.

10. Turn down current and place loaded filament in box.

14.4 Neodymium

Use outgassed single or double Re filaments.

14.4.1 Neodymium ondouble filaments

1. Using glove and tweezers, transfer the filament from the box to the loading-bay. Dismantle the filament using an allan key. Take not of which side fits where on the centre block. These must not be interchanged. Connect each side block to a separate loading connection, arranged horizontally.

2. Rinse a pipette tip with 1M HNO_3^x. Do not use phosphoric acid as this will facilitate the formation of oxides.

3. Take up a small amount of 1M HNO_3^x in the pipette and put a drop into the sample beaker. Using the pipette tip, toll drop around the bottom of the beaker so as to dissolve the sample.

4. Take up sample from the beaker with the pipette and load centrally on to filament.

5. Expel remaining sample solution back into the beaker.

6. Dry down at 1A under light. A white spot will normally be evident.

7. Reassemble the filament and return it to box using gloves and tweezers as necessary.

14.4.2 Neodymium with graphite on single filaments

Before using this technique, be sure that the Nd concentrate is in the chloride form, otherwise the graphite may be oxidised, resulting in unstable emission.

1. Using gloves and tweezers, transfer the filament from the box to the loading-bay.

2. Rinse a pipette tip with 1M HCl^x. Do not use nitric or phosphoric acid as this will facilitate the oxidation of the graphite.

3. Take up a small amount of graphite solution and place centrally on the filament under the heat lamp.

4. Take up a small amount of 1M HCl^x in the pipette and put a drop into the sample beaker. Using the pipette tip, roll drop around the bottom of the beaker so as to dissolve the sample.

5. Take up sample from the beaker with the pipette and load onto the graphite drop on the filament before the graphite dries.

6. Expel remaining sample solution back into the beaker.

7. Dry down at 1A under light.

8. Return filament to box using gloves and tweezers as necessary. Care must be exercised otherwise it is possible to knock off the carbon and hence lose the Nd load.

14.5 Lead

15 Selected isotope masses

16 Spike and natural constants

Table 3. Spike and natural constants for use at the Council for Geoscience

	natural	spike		standard
		weak	strong	
Rubidium				
$^{85}Rb/^{87}Rb$	*2.59265*	0.0081	0.028728	
^{87}Rb ppm		9.435	48.654	49.33617
Date prepared				
Strontium				
$^{84}Sr/^{86}Sr$	0.056584		18.471	
$^{87}Sr/^{86}Sr$			0.39088	
$^{86}Sr/^{88}Sr$	0.1194		3.0392	
^{86}Sr ppm			0.4224	20.60879
Date prepared				
$^{84}Sr/^{86}Sr$	0.056584		18.471	
$^{87}Sr/^{86}Sr$			0.39088	
$^{86}Sr/^{88}Sr$	0.1194		3.0392	
^{86}Sr ppm			0.4224	20.60879
Date prepared				
Samarium				
$^{149}Sm/^{147}Sm$	0.9216		299.7	
$^{152}Sm/^{147}Sm$	1.78307		2.01613	
^{147}Sm ppm			0.04488	
Date prepared				
Neodymium				
$^{142}Nd/^{144}Nd$	1.14187			
$^{143}Nd/^{144}Nd$			0.4354	
$^{145}Nd/^{144}Nd$	0.348410 $\pm$ 12		0.3858	
$^{146}Nd/^{144}Nd$	0.7219		0.951	
$^{148}Nd/^{144}Nd$	0.241587 $\pm$ 6			
$^{150}Nd/^{144}Nd$	0.236446 $\pm$ 6		108.2	
^{144}Nd ppm			0.2951	
Date prepared				

17 Useful formulae

17.1 Fractionation on TIMS

17.2 Isotope systems

17.2.1 Rb-Sr isotope decay system

17.2.2 Sm-Nd isotope decay system

17.2.3 U-Th-Pb isotope decay system

17.3 Radiogenic isotopes and mixtures

18 Data reduction and isotope dilution

18.1 Concentration measurements by isotope dilution

18.2 Boelrijk method for isotope dilution

18.3 Error propagation

18.4 Double spike calculations

Volume

6

Stable isotope mass spectrometry

19 O, D, C and N isotope techniques (to be added)

Volume

7

Bibliography

20 References

Ball, J. W. and Bassett, R. L. (2000). Ion exchange separation of chromium from natural water matrix for stable isotope mass spectrometric analysis. *Chem. Geology,* **168**, 123-134.

Crouch, E. A. C. and Webster, R. K. (1963). Choice of optimum quality and constitution of the tracer used for isotopic dilution analysis. *Journal of the Chemical Society,* **18**, 118-131.

Duval, C. (1953) *Inorganic thermogravimetric analysis*. Elsevier, Amsterdam, 531 pp.

Ellis, A. S., Johnson, T. M., and Bullen, T. D. (2002). Chromium isotopes and the fate of hexavalent chromium in the environment. *Science,* **295**, 2060-2062.

Ho, S. E., McNaughton, N. J., and Groves, D. I. (1994). Criteria for determining initial lead isotopic compositions of pyrite in Archaean lode-gold deposits: a case study at Victory, Kambalda, Western Australia. *Chem. Geology,* **111**, 57-84.

Kingston, H. M. and Jassie, L. B. (1988) . Monitoring and predicting parameters in microwave dissolution., 93-154. *In* Kingston,H.M. and Jassie,L.B. (*eds.*), *Introduction to microwave sample preparation. Theory and practice.,* American Chemical Society, Washington

Neuerburg, G. J. (1975). A procedure, using hydrofluoric acid, for quantitative mineral separations from silicate rocks. *U. S. Geol. Surv. J. Res.,* **3**, 377-378.

Richard, P., Shimizu, N., and Alegre, C. J. (1976). 143Nd/144Nd, a natural tracer: an application to oceanic basalts. *Earth Planet. Sci. Lett.,* **31**, 269-278.

Shirey, S. B., Banner, J. L., and Hanson, G. M. (1987). Cation-exchange column calibration for Sr and the REE by EDTA titration. *Isotope Geosc.,* **65**, 183-187.

Strelow, F. W. E. and Van der Walt, T. N. 1981. Highly accurate determination of trace amounts of uranium in standard reference materials by spectrophotometry with Chlorophosphonazo III after complete separation by anion and cation exchange chromatography. *Fresenius J Anal Chem* 110-4.

Strelow, F. W. E. and Van der Walt, T. N. (1979). Accurate determination of trace amounts of uranium in rocks by spectrophotometry with chlorophosphonazo III after separation by anion exchange chromatography. *S. -Afr. Tydskrf. Chem.,* **32**, 169-172.

Zindler, A. 1980. *Geochemical processes in the Earth's mantle and the nature of crust-mantle interactions: evidence from studies of Nd and Sr isotope ratios in mantle-derived igneous rocks and lherzolite nodules.* Ph.D. thesis (unpubl.), M.I.T., 263pp.