CHAPTER III

EXPERIMENTS

3.1 Sample Preparation

The sample was ground by an automatic grinder for 1 hour. The particle size was separated into different fractions: -60, -100, -200 mesh by a vibrating screen. The -100 mesh fraction was used in small scale digestions and the -200 mesh fraction was used for quantitative analyses.

3.2 Quantitative Analysis of Zircon

3.2.1 Chemical and Spectrophotometric Analyses

The sample was fused , according to H. Bennett and R. A. Reed,(21) in a platinum crucible with direct flame. The spectrophotometric determinations of silicon and iron were performed by the formation of coloured complexes with ammonium molybdate and 1:10 phenanthroline respectively.(21, 22, 23)

Apparatus
1. Platinum crucible capacity of 50 cm^3
2. Meker burner
3. pH meter (Beckman, model 28)
4. Double-Beam Grating Spectrophotometer (Perkin-ELmer Model 124) equipped with a recorder model 56

Reagent Ammonia solution, Chloroform (A. R. Grade, BDH) anhydrous potassium carbonate, Boric acid, Gelatin, Cupferron, Ammonium molybdate (Lab Grade, BDH)

anhydrous sodium carbonate, Hydrofluoric acid (48% W/W), Acetic acid (glacial), Hydrogen peroxide (A. R. Grade, Mallinckrodt)

Sulphuric acid 95.97%, Hydrochloric acid 37%

1:10 Phenanthroline für Analyse (RIEDEL-DE HAËNAG SEELZE-HANNOVER)

Potassium pyrosulphate (A. R. Grade), 2:4 dinitrophenol (Merck)

Hydroxylamine hydrochloride (Lab Grade, EASTMAN)

Deionised water

Preparation of Reagents

Ammonium acetate (approx. 10% W/V) solution

14 CM^3 of acetic acid (glacial) was diluted to 200 cm^3 with water and 14 cm^3 of ammonia solution was added carefully. The solution was mixed, cooled and adjusted to approximately pH 6.0 either with acetic acid or ammonia solution.

Ammonium molybdate (80 g/l) solution

8 G of ammonium molybdate $[(NH_4)_6 Mo_7 O_{24}.4H_2O]$ was dissolved in 100 cm^3 of water, filtered if necessary. The solution was stored in a polyethylene bottle and discarded after 4 weeks.

Cupferron (60 g/1) solution

3 G of cupferron [ammonium salt of N-nitroso-N-phenylhydroxylamine] was dissolved in 50 cm^3 of cold water and filtered. This solution must be freshly prepared.

Cupferron wash solution

100 CM^3 of hydrochloric acid was added to 800 cm^3 of water. 1.5 G of cupferron was dissolved in 100 cm^3 of cold water and filtered. The two solutions were mixed.

1:10 Phenanthroline (10 g/1) solution

0.1 G of 1:10 phenanthroline was dissolved in 10 cm^3 of diluted acetic acid (1+1).

Procedure

Decomposition of the sample

1.000 G of the finely ground, dried (110°C) sample was weighed into a platinum crucible. 5 G of fusion mixture and 2 g of boric acid was added and mixed intimately.

The mixture was heated over a mushroom burner, cautiously at first; then the temperature was gradually raised to the full of the burner for 1 hour. The crucible was removed from the burner and allowed to cool. The fusion mixture was transferred to a beaker.

15 CM^3 of diluted sulphuric acid (1+1) and 20 cm^3 of diluted hydrochloric acid (1+1) were added and the beaker was transferred to a steam bath to dissolve the melt.

Determination of Gravimetric Silica

0.5 G of gelatin was added, stirred and mixed well, ensuring that any gel adhering to the sides of the beaker was brought into contact with the coagulant. 10 CM^3 of water was added, mixed and allowed to stand for 5 minutes.

The precipitate was filtered and washed five times with hot, diluted hydrochloric acid (1+19) and then with hot water until the filtrate was free from chlorides.

The paper and precipitate were transferred to an ignited and weighed platinum crucible, then ignited at low temperature until the precipitate was free from carbonaceous matter and then heated at 1200°C to constant weight.

The content of the cold crucible was moistened with water and 5 drops of diluted sulphuric acid (1+1) and 10 cm^3 of hydrofluoric acid (48% W/W) were added successively. The mixture was evaporated to dryness on a sand bath in a fume cupboard.

The crucible and residue were heated, cautiously at first, over a gas flame and finally for 5 minutes at 1200°C. The crucible was cooled and weighed. The difference between the two weights represented the "gravimetric" silica.

Preparation of the Combined Solution of Silica Filtrate and Silica Residue

40 CM^3 of hydrochloric acid was added to the filtrate from the determination of main silica and the solution was boiled down to a volume of about 250 cm^3.

The residue from the hydrofluoric acid treatment of the "gravimetric" silica was fused with about 2 g of potassium pyrosulphate. The melt was dissolved in 10 cm^3 of water and 5 cm^3 of diluted sulphuric acid (1+1), in the crucible, over a low flame. This solution was added to the boil-down silica filtrate to form the "combined solution"

The "combined solution" was cooled to a temperature of less than 10°C in ice water. 125 CM^3 of cold cupferron solution (60 g/1) was added and slowly stirred. The beaker and contents were stood in the cold for 5 minutes. A few more drops of cupferron solution (60 g/1) was added to check that no further precipitation took place.

The solution was filtered through a no. 42 whatman paper, the precipitate was washed thoroughly with cold cupferron wash solution and transferred to a platinum crucible. The crucible was placed in an oven at 110°C until the precipitate was dried and the carbon was then burnt off at low temperature in a fume cupboard. The precipitate was ignited at 1200°C to constant weight; 30 minutes was usually sufficient.

The ignited residue was fused in a platinum crucible with 15 g of potassium pyrosulphate. The crucible was cooled and the melt was dissolved in 30 cm^3 of water and 20 cm^3 of diluted sulphuric acid (1+1) over low flame.

The solution was cooled and diluted to 100 cm^3 in a volumetric flask and mixed.

Determination of Ferric oxide

1 CM^3 aliquot of the solution of the ignited cupferron precipitates was transferred to a 100 cm^3 volumetric flask. 2 CM^3 of hydroxylamine hydrochloride solution (100g/1) and 5 cm^3 of 1:10 phenanthroline solution (10 g/1) were added. Ammonium acetate solution (approx. 10%) was added until a pink colour developed in the solution and 2 cm^3 more was added in excess.

The solution was allowed to stand for 15 minutes, after which it was diluted to 100 cm^3 and mixed.

The absorbance of the solution was measured against water in 10 mm cells at 510 nm. The colour was stable between 15 and 75 minutes after the addition of the ammonium acetate solution.

The ferric oxide content of the solution was determined by reference to a calibration curve.

Preparation of the Solution for the Determination of Residual Silica

The filtrate and washing, reserved from the cupferron precipitation was transferred to a 500 cm^3 separating funnel. 20 CM^3 of chloroform was added and the mixture was shaked vigorously. The layers were allowed to separate and the chloroform layer was withdrawn. The extraction was repeated with two further 20 cm^3 portions of chloroform and the chloroform extracts were discarded.

The aqueous solution from the extraction was transferred to a 500 cm^3 beaker and 20 cm^3 of hydrogen peroxide solution (30%) was added. The solution was boiled until it was colourless.

The solution was allowed to cool and diluted to 200 cm^3 in a volumetric flask and mixed.

Determination of Residual Silica

25 CM^3 aliquot of the solution was transferred to each of two 50 cm^3 volumetric flasks, A and B, and a few drops of 2:4 dinitrophenol indicator was added. To flask B ammonia solution was added dropwise until the indicator turned yellow (note the number of drops used) then 5 cm^3 of diluted hydrochloric acid (1+4) was added. 5 CM^3 of diluted hydrochloric acid (1+4), the same number of drops of ammonia as needed to neutralize the solution in flask B and 5 cm^3 of ammonium molybdate solution (80 g/l) were added to flask A.

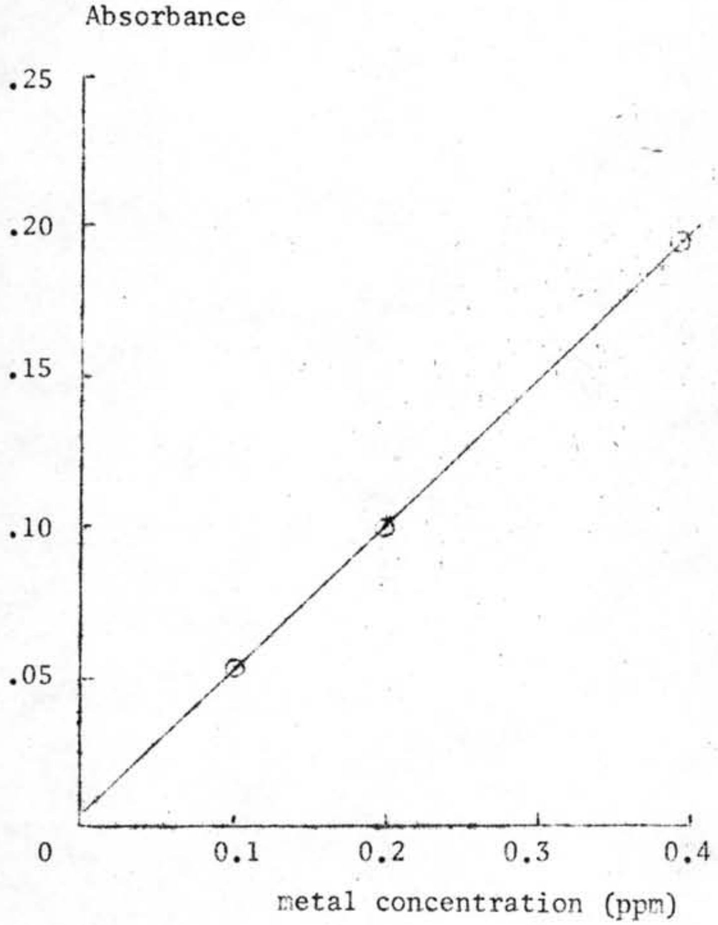
The volume of both solution were made exactly 50 cm^3 by addition of water. The silicomolybdate colour in flask A was measured against the solution in flask B in 10 mm cells at 440 nm.

The absorbance must not be measured sooner than 5 minutes and later than 15 minutes after the addition of the ammonium molybdate solution.

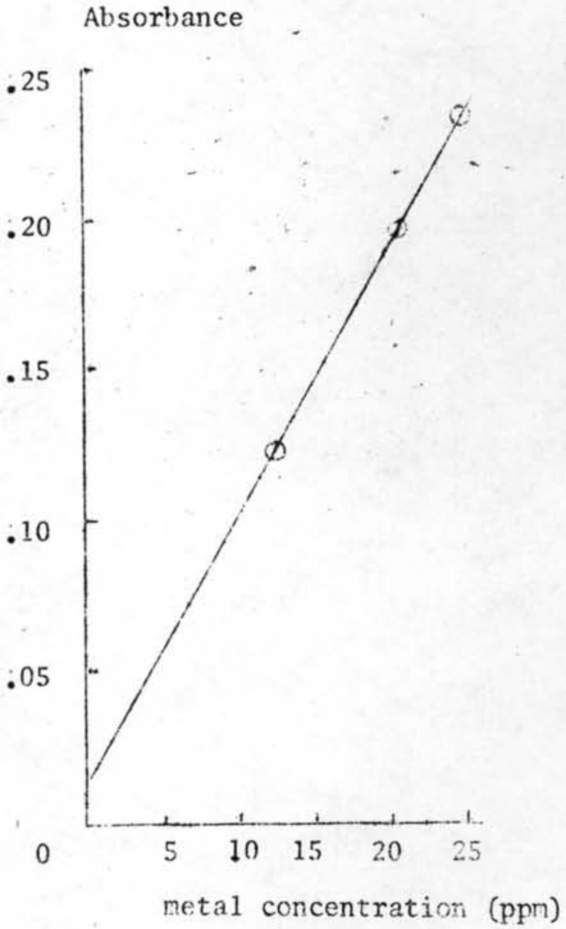
The silica content of the solution was determined by reference to a calibration curve.

Calculation of Total Silica Content

The residual content was added to the figure obtained for the "gravimetric" silica to obtain the total silica content.



Calibration curve for the determination of iron by UV-Visible Spectrophotometry



Calibration curve for the determination of silicon by UV-Visible Spectrophotometry

3.2.1 X-Ray Fluorescence Analysis

The XRF analysis system is shown schematically in Figure 3.1. The resolution of the system is 215 eV (FWHM) at 5.9 keV Mnk_{α} line. The source sample set-up is shown in Figure 3.2.

Apparatus

1. ORTEC 7000 Series Si(Li) X-Ray Detector
    - 1.1 Lithium-drifted Silicon diode 6 mm x 5.15 mm
    - 1.2 Liquid Nitrogen reservior dewar
2. ORTEC Model 459 Power Supply
3. ORTEC Model 716 A Amplifier
4. Type ND 2200 Multichannel Pulse Height Analyzer
5. Type RM 503 Oscilloscope
6. IBM Electric Typewriter
7. Annular Am-241 radioisotopic source (10 mCi)

Reagent

Zirconium oxide, Cerium oxide, Lanthanum oxide, Neodymium oxide, Ferric oxide (Spectroscopic Pure Grade, Koch-Light Laboratories, Ltd.)

Silicon dioxide, Prasyodymium oxide, Calcium oxide, Magnesium oxide (Spectroscopic Pure Grade, SPEX Industries, INC)

Aluminium oxide, Titanium oxide (A. R. Grade, SPEX Industries, INC.)

Preparation of Calibration curve

Calibration of the detector was performed by using Variable Energy X-ray Source from the Radiochemical Center, Amersham, England. A typical calibration curve at coarse gain 50, fine gain 1.0 and conversion gain 1024 was shown in Figure 3.3.

Procedure

A standard reference ore was prepared by mixing specpure oxides of the elements. The composition of the synthetic standard ore which was made nearly similar to that of the ore sample$^{(24)}$was shown in Table 3.1. The oxides were ground together for homogeneity. 15 G of ore of -200 mesh was put into a plastic container after which was placed on the X-ray source. The components of the ore was analysed by comparing the peak intensity with the corresponding peak of the synthetic standard. A counting time of 100 seconds was set in all cases.

The content of each element in a sample was calculated by the equation

$$W = W_s \cdot \frac{A}{A_s}$$

where W = Weight of element in sample

W_s = Weight of element in standard

A = Photopeak area of the element in sample

A_s = Photopeak area of the element in standard

The photopeak area was determined by Covell's method.

$$A = \sum_{i=h}^{i=r} a_i - (a_h + a_r)(r-h+1)/2$$

where

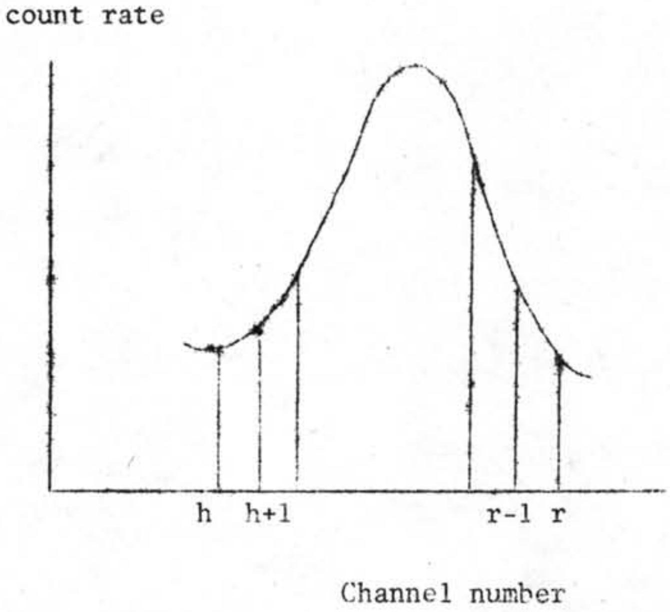
A = Photopeak area of the element

a_i = number of counts in the i^{th} channel

a_h = number of counts in the channel h

a_r = number of counts in the channel r

i, h, r = channel number at i, h and r respectively



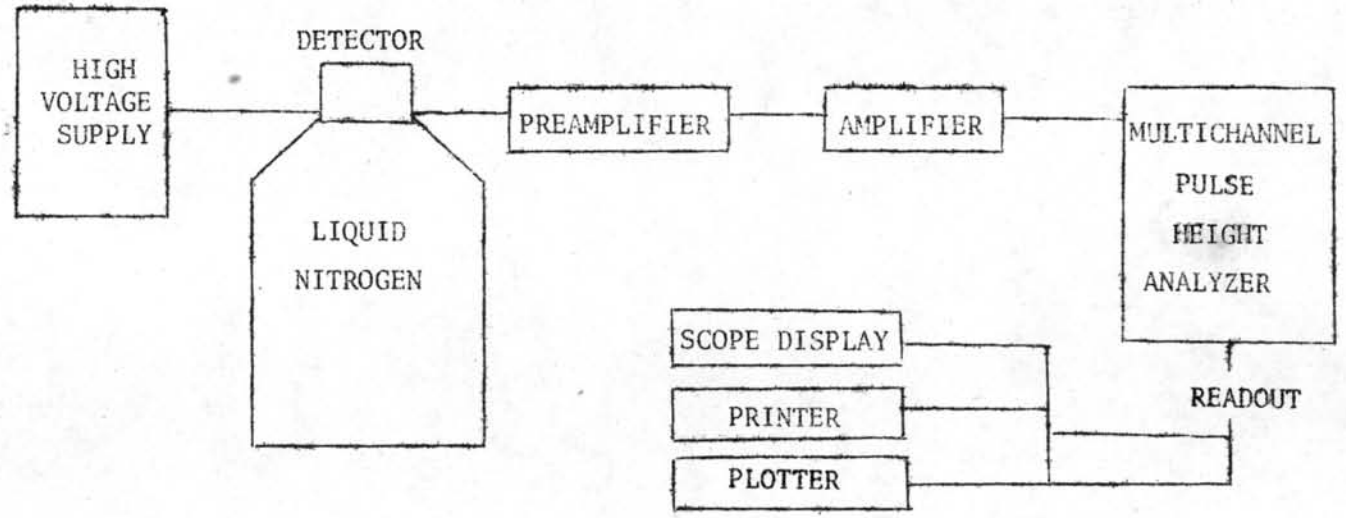
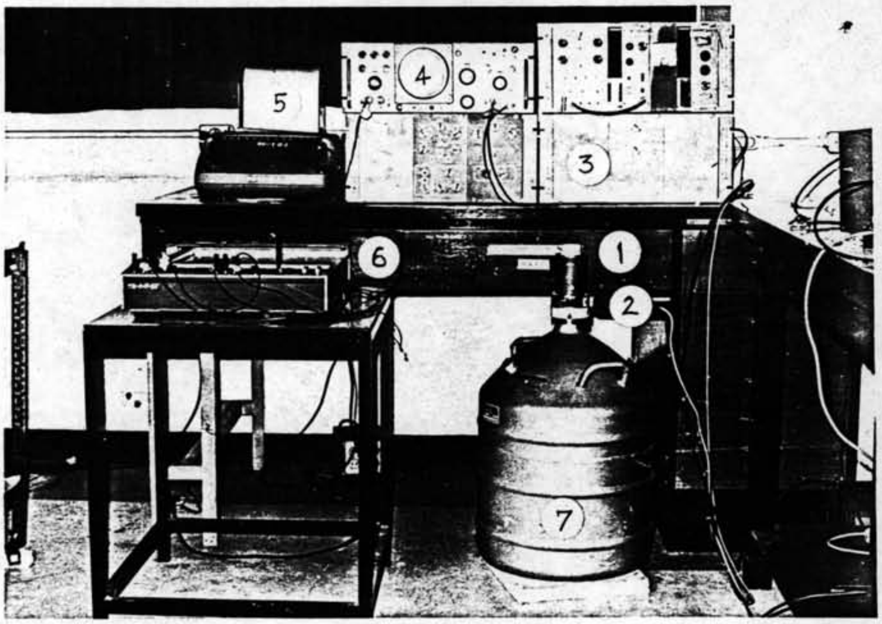


Figure 3.1 Block diagram of the X-ray/γ-ray instrument.

Figure 3.2 The set-up of the X-ray/γ-ray instrument.



1. Sample
2. Detector
3. Multichannel Analyzer
4. Scope Display
5. Printer
6. Plotter
7. Liquid Nitrogen Dewar

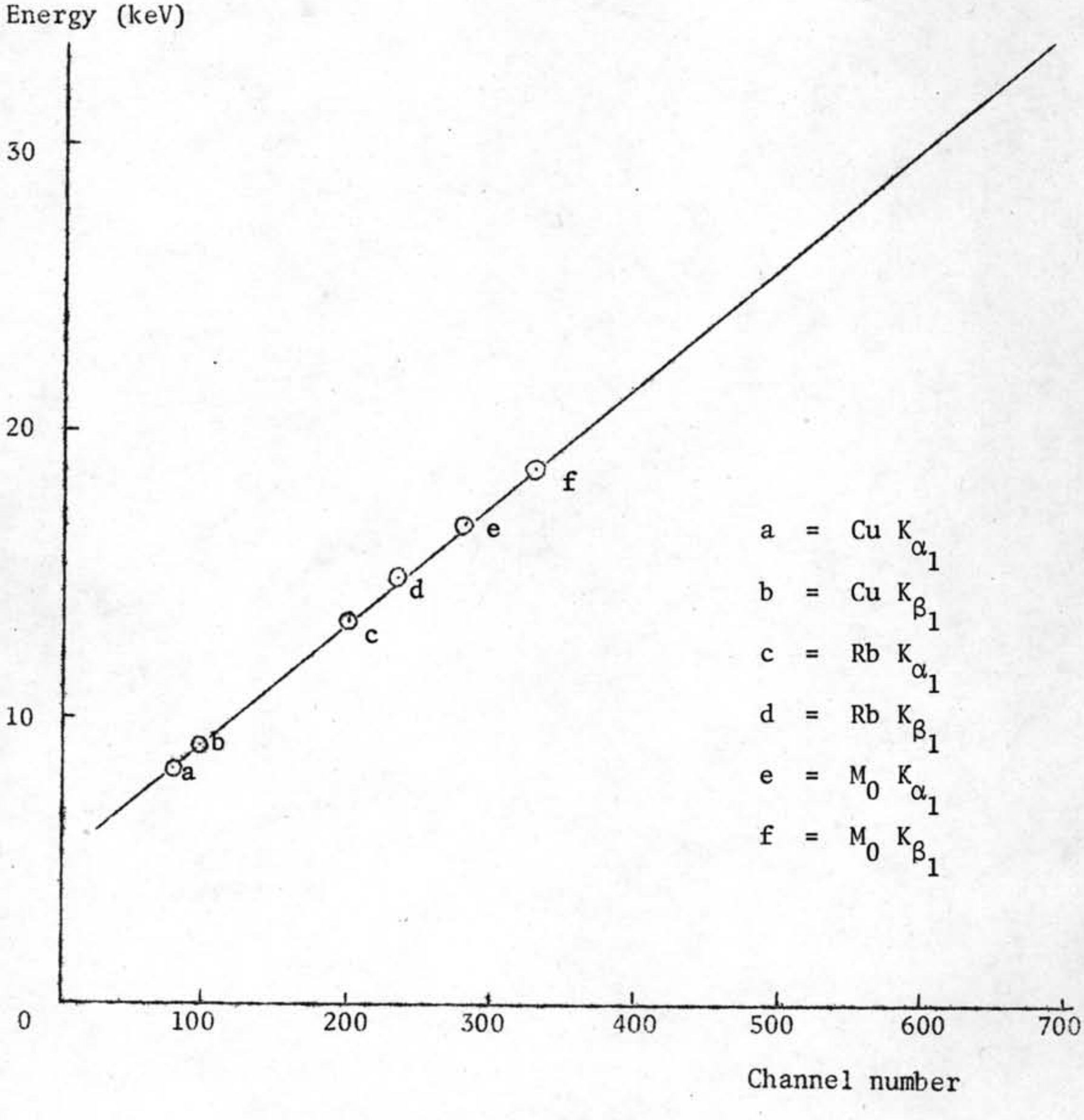


Figure 3.3 Calibration curve of the Si(Li) Detector

at gain 50/1.0

Table 3.1 Composition of the standard ore(24)

Component	weight (g)	%
ZrO_2	8.250	55.00
SiO_2	4.500	30.00
CeO_2	0.300	2.00
La_2O_3	0.150	1.00
Pr_2O_3	0.075	0.50
Nd_2O_3	0.075	0.50
TiO_2	0.750	5.00
Fe_2O_3	0.300	2.00
CaO	0.225	1.50
MgO	0.225	1.50
Al_2O_3	0.150	1.00
Total	15.00	100.00

3.2.3 Instrumental Neutron Activation Analysis (INAA)

Various elements can be made radioactive by bombardment with neutrons. The emitted gamma rays from the (n, γ) reaction can be used in qualitative and quantitative analyses. The amount of radioactivity produced can be calculated from the equation:

$$A = \frac{N_o W f \sigma \phi (1-e^{-\lambda t})}{At.Wt}$$

where A = induced activity at the end of irradiation (dps)
σ = cross section of an element (cm^2/atom)
ϕ = thermal neutron flux (n/cm^2 s)
t = irradiation time
λ = decay constant of product nuclide = $0.693/T_{1/2}$
$T_{1/2}$ = half-life of product nuclide
W = weight of element (g)
f = fractional isotopic abundance of the target nuclide
N_o = Avogadro's number
At.Wt. = atomic weight of the element

Theoretically, it is possible to calculate the quantity of various elements present in a sample from the above equation. In practice, however, the absolute activity cannot be determined easily since the exact value of ϕ and σ are not known . For this reason, the comparative method is generally used. That is to compare the activity of the sample with a standard whose compositions and concentration are exactly known. Thus, the quantity of each element in a sample can be calculated by the equation:

$$\frac{\text{weight of element in sample}}{\text{weight of element in standard}} = \frac{\text{count rate of sample}}{\text{count rate of standard}}$$

Apparatus Energies which are lower than 100 keV were detected with a HpGe detector with 25 mm^2 active area. The resolution of the system is 178 eV (FWHM) for the 122 keV Co-57 line.

1. Canberra 7100 Series HpGe Detector
2. Canberra Model 2000 Power Supply
3. Canberra Model 1713 Amplifier
4. Canberra Model 410 Linear Amplifier
5. Teletype Model 33
6. X-Y Recorder OMNIGRAPHIC Series 2000

Energies which are higher than 100 keV were detected with a Ge(Li) detector with 18.1 cm^2 active area. The resolution of the 122 keV gamma line of Co-57 is 500 eV (FWHM)

1. Canberra 7000 Series Ge(Li) Detector
2. Canberra Model 3005 Power Supply
3. Type RM 503 Oscilloscope
4. Digital pdp 8/e
5. Teletype Model 33

Reagent Silicon dioxide, Uranium oxide, Prasyodymium oxide, Tantalum oxide, Thorium oxide (Spectroscopic Pure Grade, SPEX Industries, INC)

Titanium oxide, Aluminium oxide (A.R. Grade, SPEX Industries, INC.)

Lanthanum oxide, Ferric oxide, Cerium oxide, Neodynium oxide, Hafnium oxide, Zirconium oxide (Spectroscopic Pure Grade, Koch-Light Laboratories, Ltd.)

Preparation of Calibration curve

Calibration of the detector was performed by using Na-22, Co-60 and Cs-137. A typical calibration curve was shown in Figure 3.4.

Procedure

The specpure grade oxide were used as standard. The samples together with standards, 0.1 and 0.005 g respectively, were sealed in 1 cm^3 polyethylene vials and subjected to irradiation in the core of the Thai Research Reactor-1/Modification (TRR/1) for 20 minutes. The neutron flux in the core was approximately 10^{13} n/cm^2s.

The concentration of uranium and thorium as impurities in the final products were determined by irradiation of the sample in the pneumatic tube system. The photopeak at 29.2 keV and 74.7 keV were counted immediately after irradiation for 100 seconds. The neutron flux in the irradiating position was approximately 10^{12} n/cm^2s. The half-life, irradiation-time, decay time and the gamma energies of the radioactive nuclides used are summarised in Table 3.2

Table 3.2 Half-life, gamma energies, irradiation and decay time of the radioactive nuclides

Element	Radionuclide	Half-life	Irradiation time	Irradiation Position	Decay time	γ-Ray (keV)
Al	Al-28	2.25 m	2 m	Pnuematic	3 m	1779
Ti	Ti-51	5.8 m	3 m	Pnuematic	3 m	320,928
Zr	Zr-95	65 d	20 m	Rotary Specimen Rack	27 d	724,756,766
					32 d	724,756,766
				Rotary Specimen Rack	40 d	724,756,766
La	La-140	40.22 h	20 m	Rotary Specimen Rack	1 d	1595.4
					3 d	486.8, 815.5
Ce	Ce-141	32.5 d	20 m	Rotary Specimen Rack	8 d	145.4
	Ce-143	33 h			3 d	293.1
Pr	Pr-142	19.2 h	1 h	Pnuematic	1 d	1575.5
Nd	Nd-147	11.01 h	20 m	Rotary Specimen Rack	8 d	91.4, 531
Hf	Hf-181	42 d	20 m	Rotary Specimen Rack	20 d	482,346
					27 d	482,346
					32 d	482,346
Ta	Ta-182	16 m	3 m	Pnuematic	3 m	172,147,185
Th	Th-233	22.3 m	3 m	Pnuematic	3 m	29.2
U	U-239	23.5 m	3 m	Pnuematic	3 m	74.7

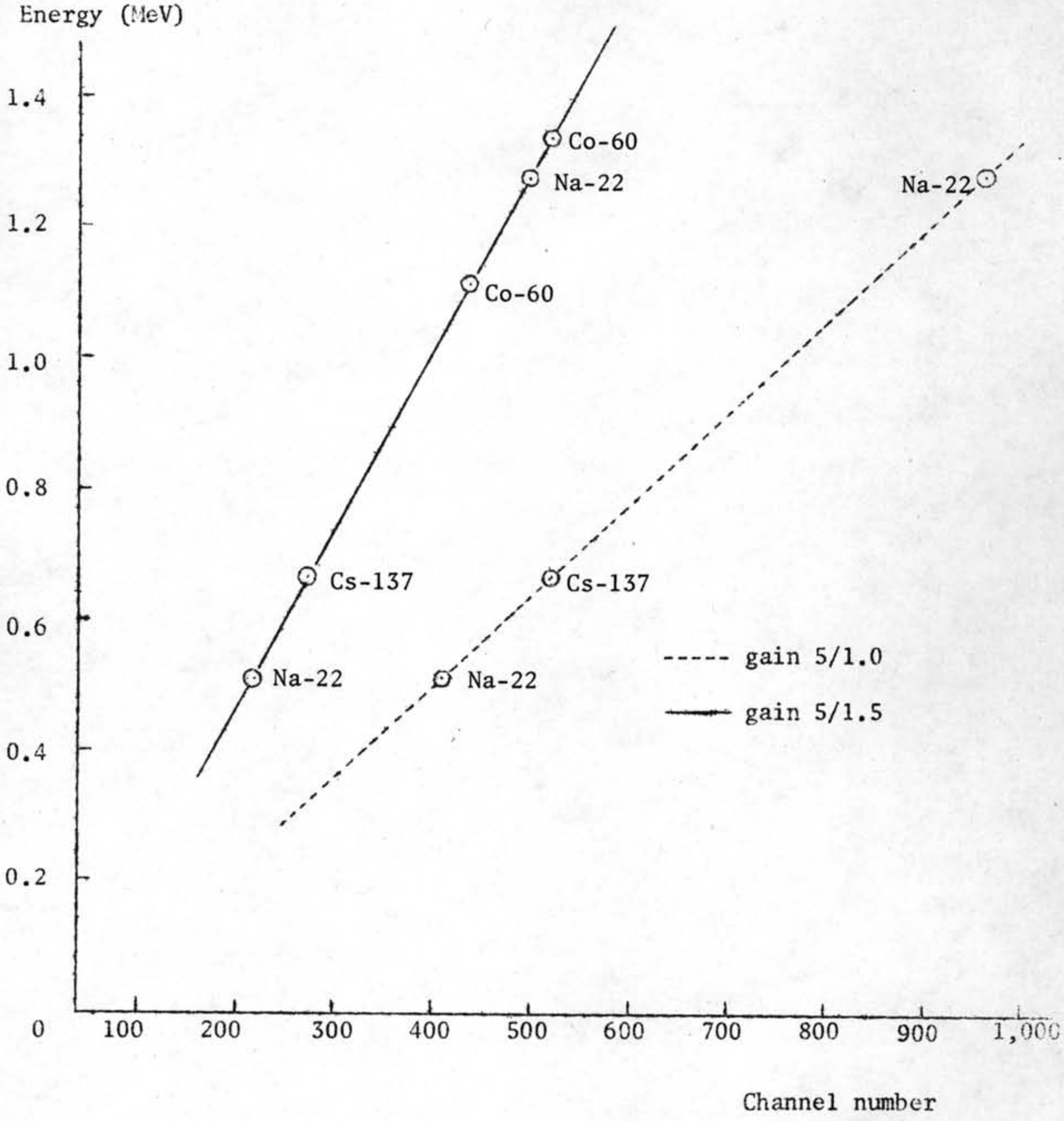


Figure 3.4 Calibration curves of the Ge(Li) detector

3.3 Alkali Fusion of Zircon

The flow diagram in Figure 2.1 was followed. In order to obtain the optimum conditions for the alkali fusion of zircon, the effect of the caustic soda to sand ratio, the reaction temperature, the time of reaction and the particle size were studied by using 3 g zircon per batch. Having selected the optimum conditions, a number of trial experiments was performed on a larger scale by using 50 g per batch.

In the case of small scale digestion, the reaction was allowed to take place in a 100 cm^3 stainless steel beaker and the mixture was dehydrated at $300^{o}C$ in a furnace for 1 hour to produce a cake which was then fused at $700^{o}C$ in the same furnace for 1 hour. After fusion, the cake was leached with ten times its weight of water to remove the excess sodium hydroxide and water soluble sodium silicate.(16, 26) The washed cake was dried at $110^{o}C$ and then dissolved in concentrated hydrochloric acid at $80\text{-}95^{o}C$, followed by slow stirring for about 20 minutes. The silicic acid was coagulated by the addition of a small amount of gelatin (0.8 g per litre). The insoluble residue which contained the undigested ore and the coagulated silicic acid was filtered from the solution. When the solution was cooled to room temperature, zirconyl chloride octahydrate crystallized out. The crystals were washed with concentrated hydrochloric acid, filtered and dried at $85^{o}C$.(4) Zirconyl chloride octahydrate was dissolved in water and precipitated as zirconium hydroxide when the pH of the solution was adjusted to

4.5 by the addition of sodium hydroxide solution. The hydroxide was dissolved in nitric acid for the subsequent step of purification. Similar process was performed on 50 g/batch digestion by using 500 cm^3 stainless steel beaker as reaction vessel.

3.4 TBP Extraction

To obtain the optimum condition for solvent extraction the effect of metal ion concentration, TBP concentration, extraction-time and the amount of salting out agent were investigated. The nitric acid concentration was fixed at 5.3 mol/l.(8, 13) Higher concentration of nitric acid results in higher distribution coefficien (K_d) but is not economically feasible. The salting out agent used was sodium nitrate.(9, 12, 13) The aqueous feed was prepared by dissolving standard zirconyl chloride into the appropriate amount of 5.3 mol/l HNO_3. The solvent used was TBP in kerosene which was previously saturated with 5.3 mol/l HNO_3. 10 CM^3 of the feed solution was mixed with 10 cm^3 of TBP in kerosene and the solution was shaken by an automatic shaker at room temperature (30°C). The organic phase was then stripped with 10 cm^3 water. After extraction, a certain volume of the aqueous phase was analysed by X-ray fluorescence. The distribution coefficient was evaluated as the ratio of the metal concentration in the organic phase to the concentration in the aqueous phase. The optimum extraction conditions were applied to the extraction of zirconium from the digestion solution. The organic phase was scrubbed twice with a 3.5 mol/l $NaNO_3$-5.3 mol/l HNO_3 mixture prior to stripping with water.