CONCENTRATION OF URANIUM CONTENT OF
THE BLACK SEA SEDIMENTS USING FROTH FLOTATION

by

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ÖZET

Karadeniz dip çökeltisi üzerinde yapılan araştırmalar bu sedimentlerin uranyum içerdiğini göstermiştir. Uranyum içeren minerallerin uranyum metali eldesinde kullanılmak üzere gang'dan ayırmak için genellikle hidrometalürjik yöntemler uygulanır. Karadeniz dip sedimentlerinde uranyum konsantrasyonu çok düşük olduğundan doğrudan hidrometalürjik yöntemlerin seçilmesi kullanılan madde miktarlarının çok artmasına sebep olur. Bunun önüne geçmek için bu tez çalışmasında bir fiziksel ön zenginleştirme işlemi olan flotasyon uygulayarak uranyum bakımından zengin bir konsantre elde edilmesi üzerinde çalışılmıştır. Flotasyon denemelerinde bu çalışmada belirtilen reaktifler ile pH, reaktif miktarı ve pülp yoğunluğu değiştirilerek flotasyona olan etkisi araştırılmıştır.

Dip çökeltisinin ve flotasyon sonucu elde edilen artık ve konsantrenin uranyum analizlerinde spektrofotometrik metod seçilmiştir.

Deneysel sonuçlara göre en yüksek randıman değeri olarak % 31.8 elde edilmiştir. Bu sonucun eldesinde 0.01148 gr Na_2SiO_3'e 17 dakika, 0.01 gr $FeCl_3$'e 15 dakika ve belirli bir kollektör reaktif karışımına 60 dakika kıvamlaştırma süresi uygulanmıştır. Pülp yoğunluğu % 20, ortam pH'sı 8 ve flotasyon süresi 5 dakika seçilmiştir.

ABSTRACT

The recent studies about The Black Sea Sediments showed that it contains trace amounts of uranium. In the production of uranium metal, uranium minerals are separated from gange minerals by hydrometallurgical processes. Since the Black Sea Sediments have very low uranium content the direct application of hydrometallurgical processes increases the reagent amounts. To overcome this problem, in this thesis work application of flotation in order to obtain a concentrate which will be rich in uranium content is studied. In flotation experiments the effect of changes of pH, the quantity of flotation reagents and pulp density on uranium concentration were studied.

A method of uranium analysis based on spectrophotometry was chosen for the analysis of the sediments tailing and concentrate.

The highest yield obtained was 31.8 %, and this recovery was obtained using 0.01148 gr Na_2SiO_3 with 17 minutes conditioning time, 0.01 gr $FeCl_3$ with 15 minutes conditioning time and a mixture of aeropromoter reagents with 60 minutes conditioning time. The other parameters were chosen as follows: Pulp density 20 %, medium pH 8 and flotation time 5 minutes.

KEY WORDS

Uranium, deposits, production, analysis, determination by spectrophotometry, flotation.

ACKNOWLEDGEMENTS

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CHAPTER I
INTRODUCTION

Today's World energy production (especially electrical
energy) mainly depends on the fossil fuels (oil, coal,
natural gas) and hydroelectric energy. Fossil fuel resources
are limited. Futhermore these resources of fossil fuels are
very valuable as raw material for the chemical industry and
for metallurgical purposes.

Therefore the main aim for the present day electrical
energy production has become to use solar, wind, ocean,
geothermal, nuclear and thermonuclear energy where nuclear
energy is the only one which is, technologically developed
and available. The only major drawback it seems to
have is the radioactive wastes it produces.

For the energy shortage in Turkey the estimates show
that the resources of fossil fuels for the thermoelectric
power plants and hydroelectric potential for the hydroelec-
tric power plants will become insufficient by the end of
1995 s, and there will be an energy shortage until the year
2000. Since Turkey has some climatic advantages solar energy
may be an alternative source, but for the present solar
energy is a developing branch of the engineering. Therefore
nuclear energy seems the only alternative which will give
results in a short time.

The fuels that could be used in nuclear energy produc-

tion are Uranium and Thorium. Natural uranium contains isotopes which are fissionable U-238 (about 99.3%), fissile U-235 (about 0.71%) and U-234 (trace amount). U-235 is defined as fissile nuclide because it has high probability of having a fission reaction with slow neutrons while U-238 can have a fission reaction with neutron energies above 10 MeV. Thorium is a fissionable nuclide, it can undergo fission only with fast neutrons with low reaction probability. It is better to convert thorium to U-233 which is a fissile nuclide before using it in a nuclear power plant. But properties of the element and some characteristics of the conversion process makes it difficult to use as a fuel for the present day.

Since Turkey does not have high grade uranium resources (containing 0.01-3% of uranium), use of nuclear power plants will lead to dependence on imported uranium. Therefore, further study is necessary for Turkey's uranium potential.

Turkey has a reserve of about 5000 tons of uranium. Coal and phosphate ores also contain considerable amount of uranium, but the mining of these ores are not economic at present (Turkey has rich coal and phosphate ores).

Another resource which became important in the recent years and that Turkey also could use is the Black Sea sediments which have a relatively low uranium content. There are contradictions among various studies about the uranium content of these sediments. Reported values are 35 μgU/g (RI 75), a mean value of 25 ppm (DE 77) and a distribution between 1-12 ppm of uranium(3). The distribution of uranium in the Black Sea sediments follows closely the currents of the Black Sea(3). There are two main currents in the form of two circles apart from each other (resembling number eight) on about 34 degrees longitude. Sediments with high concentrations are met mostly in the center of these currents(3), and

decreases gradually towards the shoreline.

The major problem in the processing of the Black Sea mud is the transportation of the mud to the surface from a depth of about 2000 m to the fabrication site. Since the uranium concentration is very low, this will mean the transportation of gangue material. As will be discussed in chapter 3 uranium could be produced in various ways. The processes given in chapter 3 are mainly applied to uranium ores which are economically important. Because Black Sea sediments contains traceamounts of uranium it is necessary to apply one of the pre-separation and pre-concentration methods in situ as indicated in chapter 3. Froth flotation seems to be the most suitable process because the sediment has a very low mesh size and according to a hypothesis (DE 77) uranium is concentrated due to the uptake of the micro-organisms and is mainly bound to the organic matter. Thus, the ore could be separated and concentrated by using flotation, and this is the subject of this thesis study.

In the second chapter a description of deep sea sediments and Black Sea sediments are given. The production of uranium is described briefly in the third chapter. The methods of uranium analysis are discussed in the fourth chapter. The theory of froth flotation and reagents used in a flotation operation is given in the fifth chapter. In the sixth chapter the analysis of the sediment, concentrate and tailing with spectrophotometric method is described. In the seventh chapter the results and their discussion is given. The eighth chapter includes the conclusions and recommendations for further work.

CHAPTER 2
GEOLOGY OF THE BLACK SEA

In this chapter a brief description of Black Sea is
given and types of deep sea sediments are discussed in
general. This is followed by the description of the distribu-
tion and concentration of uranium among various sediment
types. The last part describes the nature and properties of
the Black Sea sediments and the elements present in these
sediments.

2.A. THE BLACK SEA SEDIMENTS

The Black Sea, which is situated between Europe and
Asia, is the largest anaerobic water body in the world. It is
surrounded from south and southwest by Turkey, from the west
by Bulgaria and Romania and from the north and east by USSR.
The Black Sea covers an area of about 423000 km^2 and has a
volume of about 540000 km^3. It has a maximum depth of 2206 m
(RI 75).

2.A.i. Main Constituents of Deep Sea Deposits

a) Biogenous Deep Sea Deposits

These are coccolithophorids, calcareous forammifera,
pteropods, radiolaria, diatoms, silicoflagellates, fish
debris, agglutinated forams, organic matter.

b) Terrigenous Deep Sea Deposits

These are quartz, feldspar, mica, clay minerals, heavy minerals, iron oxide, rock fragments, plant debris.

c) Authygenic Deep Sea Deposits

These are silicates (zeolites, clay minerals), heavy metal sulfides (Fe, Zn, Cu, Ni, Co, Pb), sulfates (Ba, Sr), carbonates (Ca, Mg, Mn, Fe), phosphates (fluorspar, apatite).

d) Volcamogenic Deep Sea Deposits

Volcanogenic glass and palagonite, pumice and other rock fragments are included in this group.

e) Cosmogenic Deep Sea Deposits

This group contains only meteoritic spherules (BU 74).

2.A.ii. Uranium in Deep Sea Sediments

Measurements made for uranium in deep sea sediments indicated a range of about 0.2-30 µg/g (RI 75) with an average value of 2 µg/g which can be taken as a representative value for deep sea sediments. The carbonate fraction in pelagic sediments can be taken as a diluting material for low uranium content that coccoliths appear to have at about 0.1 µg/g level. Concentrations of 32 and 60 µg/g have been reported for the Baltic Sea and the Norwegian sediments (RI 75) and 35 µg/g for the Black Sea sediments (RI 75). Examinations in anoxic environments shows a positive correlation between uranium and organic carbon in sediments. It is hypothesized that organic carbon material is involved in the uranium up-take. Very high uranium concentrations are observed in authy-genic phosphate minerals and skeletal apatite, with a range

of 6-524 µgU/g (RI 75). Another important deposit is fish teeth which falls in the range of 21-49 µg/g (RI 75) in uranium content, that these values are relatively higher when compared to other living material. Also fish bone material, oozes rich in diatoms shows concentrations of up to 700 µgU/g (RI 75).

2.A.iii. Properties of Black Sea Sediments

The Black Sea basin has a sediment thickness in excess of 15 km that has been accumulated for 200 million years (RO 78). Black Sea has a sedimentation rate of about 10 cm/1000 yr.

There are three main stratigraphic units that are deposited over the last 25000 years (RO 78).

A- This unit is about 30 cm thick and there are alternating white and black layers between 50 and 100 per cm. It contains as high as 80% $CaCO_3$ which is of biogenic origin. This unit contains coccolith which is rich in U_3O_8 (DE 77). The age of this unit is measured as 3000 years BP (before present).

B- This unit is about 40 cm thick, rich in organic matter (sapropel) about 50%. The age of this unit is about 7000 years BP.

C- This unit contains an alternating sequence of light and dark lutite which is poor in U_3O_8 content. The dark layers are of iron sulphide.

2.A.iv. The Elements Found in Black Sea Sediments

According to previous analysis the elements found in the Black Sea sediments are shown on a periodical table on Fig 2.1(2,3).

Fig.2.1- Elements found in the Black Sea sediments(2,3). p: Elements present in sediments.

CHAPTER 3
URANIUM PRODUCTION

In this chapter, the mineral dressing processes applicable to uranium ores, hydrometallurgical operations in the production of uranium from the ores and separation processes, such as solvent extraction and ion exchange, to obtain pure uranium compounds and metal preparation or fluorination step before fuel element fabrication is described briefly.

The production of uranium basically follows a procedure of mineral dressing, leaching, separation from leach liquor and production of metal.

3.A. PHYSICAL PRECONCENTRATION

Physical preconcentration is used if it is possible and necessary to separate the gangue from the mineral to be able to reduce excess reagent losses(4) (HE 76). The processes that are suitable for uranium minerals are as follows.

a) Sifting Separation

This is also called granulometric separation. The process works by using vibrating secreens, making use of the difference in the shapes of the useful mineral and gangue particles or making use of the differences in resistance for crushing and grinding.

b) Gravimetric Separation

Shake tables and vibrating tables gave good results for uranothorianite and monazite sand.

c) Heavy Medium Separation

For this process organic solvents with different densities are used. This separation is applied to Spanish lignites and Shells in Sweden.

d) Flotation

Phosphate-bearing minerals and pitchblend containing minerals have been processesed in this way.

e) Electromagnetic Separation

This type of separation is applied to monazite sand to separate ilmenite. This separation process is also used for davidite minerals in Australia.

f) Electrostatic Separation

This process is used to separate monazite from zircon.

3.B. LEACHING

Leaching is applied as acid leaching or as alkali leaching depending on the type of the ore that is worked on. The ore must have a mesh size of 28-200 mesh to improve leaching efficiency, however higher mesh sizes increase the viscosity of the pulp and it leads to difficulties, for example in the filtration of leach liquor after leaching operation. Leaching is applied as agitation leach or percolation leach. In agitation leach the liquids and solids are

mixed continuosly and the ore must have low mesh size. In percolation leach low mesh size is not necessary. The ore is ground to a predetermined size and filled in to special · tanks. The leach liquor is fed upwards or downwards in these tanks.

3.B.i. <u>Acid Leaching</u>

This is often used in presence of an oxidant to insure that uranium is in hexavalent state because tetravalent uranium isn't easily soluble. Oxidizing reactions are as follows (GI 63).

$$2Fe^{2+} + MnO_2 + 4H^+ \rightarrow 2Fe^{3+} + Mn^{2+} + 2H_2O$$

$$6Fe^{2+} + ClO_3^- + 6H^+ \rightarrow 6Fe^{3+} + Cl^- + 3H_2O$$

$$UO_2 + 2Fe^{3+} \rightarrow UO_2^{2+} + 2Fe^{2+}$$
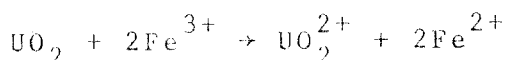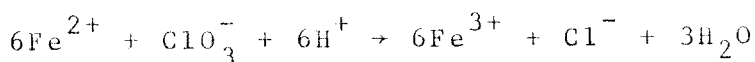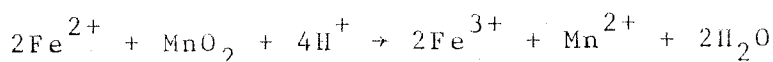
Mostly used leaching agent is sulphuric acid because of its low price and reduced corrosive properties. The reactions are (GI 63).

$$UO_3 + 2H^+ \rightarrow UO_2^{2+} + H_2O$$

$$UO_2^{2+} + SO_4^{2-} \rightarrow UO_2SO_4$$

$$UO_2SO_4 + SO_4^{2-} \rightarrow \{UO_2(SO_4)_2\}^{2-}$$

$$\{UO_2(SO_4)_2\}^{2-} + SO_4^{2-} \rightarrow \{UO_2(SO_4)_3\}^{4-}$$
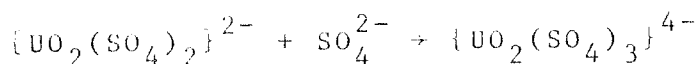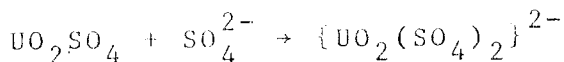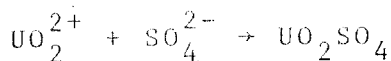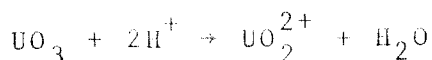
Other leaching agents are hydrochloric and nitric acids. Main parameters for the leaching are, concentration of the reagent, temperature, pressure, time and peripheral area of the solid.

3.B.ii. Alkali Leaching

This procedure is usually used if the gangue is limestone or other material easily decomposed by acid thus leading to an increase of acid consumption. Leaching solutions are sodium carbonate, sodium bicarbonate mixture, where the latter prevents uranium precipitation owing to excessive alkalinity. Air or oxygen is employed as an oxidant to ensure that the uranium is present in the hexavalent soluble condition. The reactions are (GI 63).

$$2U_3O_8 + O_2 + 18Na_2CO_3 + 6H_2O \rightarrow 6Na_4UO_2(CO_3)_3 + 12NaOH$$
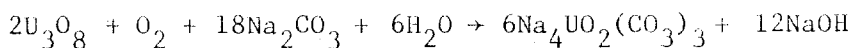
Neutralization of hydroxide is essential otherwise sodium diuranate precipitates as follows.

$$2UO_2(CO_3)_3^{4-} + 6OH^- + 2Na^+ \rightarrow Na_2U_2O_7\downarrow + 6CO_3^{2-} + 3H_2O$$
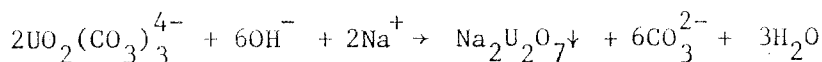
For this reason addition of an acid cation such as bicarbonate is necessary during leaching.

3.C. SEPARATION PROCESSES

Leaching liquor is filtered and ion exchange or solvent extraction is used to separate uranyl salts from others in the leach liquor. Solvent extraction is preferable when large amounts of metal is to be separated, and ion exchange is preferable when small quantities or low concentrations of metal is present.

3.C.i. Ion Exchange

Ion exchangers are materials which exchange reversibly ions that they contain with the ions in a solution, while they remain insoluble in the solvents (KE 69). Ion exchange is considered in two separate processes as cation exchange and anion exchange. Methods based on the cation exchange are

used less frequently because the most common cation exchange
resins show only little selectivity towards the uranyl ion,
however anion exchange resins show a selectivity towards
uranyl complexes especially anionic sulphate complexes of the
form $\{UO_2(SO_4)_2\}^{2-}$ and $\{UO_2(SO_4)_3\}^{4-}$, (GI 63). The reaction
of adsorption for a quaternary anion exchange is (GI 63)

$$4\{R-N(CH_3)_4 \ X^-\} + \{UO_2(SO_4)_3\}^{4-} \rightleftharpoons \{R-N(CH_3)_4\}_4 \ UO_2(SO_4)_3 + 4X^-$$
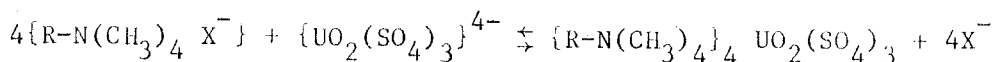
where X^- denotes Cl^- or NO_3^-

In the case of a pregnant carbonate solution (GI 63)

$$UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons \{UO_2(CO_3)\}_3^{4-}$$

and adsorption reaction is

$$4R^+ \ X^- + \{UO_2(CO_3)\}_3^{4-} \rightleftharpoons (R_4^+) \ \{UO_2(CO_3)\}_3^{4-} + 4X^-$$
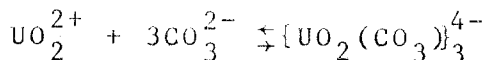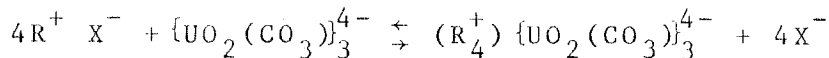
Typical elution solutions are nitric acid-ammonium
nitrate mixture or sulphuric acid-sodium chloride mixture,
where elution process works as the opposite of adsorption
reaction.

3.C.ii. Solvent Extraction

Solvent extraction is a process in which a substance
is transferred from one liquid phase into another (KE 69).
The two liquid phases are reasonably insoluble between each
other. The solvent used depends on the metallic impurities
associated with uranyl salts. Some of the common solvents are
mono and di alkyl esters of phosphoric acid, ketones and
chelates (KO 69). Uranium is Stripped from the solvent by
backwashing with hydrochloric acid, sodium carbonate etc.

One of the famous proceses that is used in uranium technology is called the Amex process and works as follows (Gl 63).

Extraction: Alkyl amines are used

$$(R_3NH)_2SO_4(org) + UO_2(SO_4)_2^{2-} (aq.) \rightleftharpoons (R_3NH)_2UO_2(SO_4)(org) + SO_4^{2-} (aq.)$$
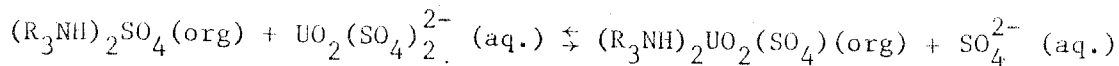
Stripping: Nitrate, chloride or carbonate solution is used

$$(R_3NH_2)_2UO_2(SO_4)_2(org) + 2NO_3^-(aq.) \rightleftharpoons 2(R_3NH)NO_3(org) + UO_2^{2+}(aq.) + 2SO_4^{2-}(aq.)$$

$$(R_3NH)_2UO_2(SO_4)_2(org) + 4Na_2CO_3(aq.) \rightarrow 2R_3N(org) + Na_4UO_2(CO_3)_3(aq.)$$

$$+ 2Na_2SO_4(aq.) + H_2O + CO_2$$
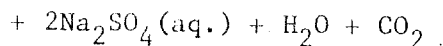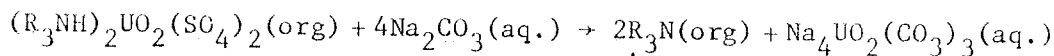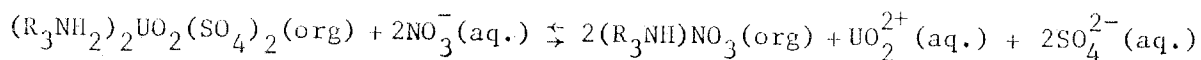
3.D. METAL PREPARATION

The uranyl complex is precipitated from the leach liquor or eluent solution or stripping solution (whether solvent extraction and/or ion exchange process is applied or not). Then uranium is precipitated from the solution (BE 57). Precipitation is applied by using NH_4OH as follows:

$$2UO_2(NO_3)_2 + 6NH_4OH \rightarrow (NH_4)_2U_2O_7\downarrow + 4NH_4NO_3 + 3H_2O$$
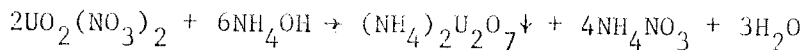
The precipitate is calcined in air to obtain UO_3

$$(NH_4)_2U_2O_7 \rightarrow 2NH_3 + H_2O + 2UO_3$$
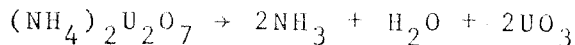
UO_3 is then reduced to UO_2 with H_2

$$UO_3 + H_2 \xrightarrow{600^{\circ}C} UO_2 + H_2O$$
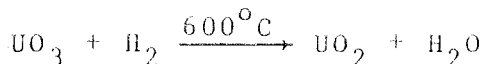
UO_2 can be used in oxide form or could be reduced to metallic form or could be converted to hexafluoride compound for isotopic enrichment.

Reduction to metallic form can be obtained as follows (KA 61)

$$UO_2 + (Mg \text{ or } Ca) \rightarrow U + (Mg \text{ or } Ca) O_2 + ZCal$$

or UO_2 can be converted to its halide salt and electrolytic reduction is applied.

For isotopic enrichment, UF_6 is prepared which is volatile at room temperature. Reactions are

$$UO_2 + 4HF \xrightarrow{550^{\circ}C} UF_4 + 2H_2O$$

$$UF_4 + F_2 \xrightarrow{350^{\circ}C} UF_6$$
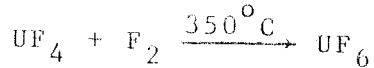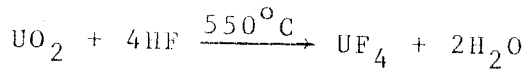
CHAPTER 4
ANALYTICAL CHEMISTRY OF URANIUM

The application of an analysing method was needed for the analysis of the sediment, tailing and concentrate. The most appropriate method was chosen among various procedures as a result of a detailed examination which makes the subject of this chapter. The methods are classified from the one which is usually used for high concentrations to the methods used for determination of trace amounts. In the second part of this chapter a detailed description of spectrophotometric method is given because it was chosen as being suitable as described in chapter 6.

Investigation and research done in recent years have facilitated the analytical chemistry of uranium, but for sensitive and reliable results nearly all methods need a pre-separation and pre-concentration. The analytical methods usually applied are as follows.

4.A. GRAVIMETRIC METHOD

This method is not suitable for determining trace amounts of uranium and is applicable to ores or solutions where uranium is the dominant element otherwise it is necessary to separate and concentrate the element quantitatively. The usual weighing form is U_3O_8 compound, therefore the precipitate obtained as a result is ignited to about $900^\circ C$ and than weighed (KO 62).

4.B. TITRIMETRIC METHOD

If gravimetric method is not suitable for analysis because either it is not possible to apply or it needs a long time for separation and ignition, a titrimetric method is usually preferred. One can obtain high precision only by using common glassware. Most common used titrimetric methods for uranium are oxidation and reduction procedures. Precipitation titration and complex formation titration are nonspecific for uranium. Titrimetric methods are also preceded by a separation procedure from interfering elements (KO 62).

4.B.i. Oxidation Procedure

This method uses the oxidation of lower valency states of uranium to U(VI), therefore oxidation is preceded by reduction of uranium to U(IV) or to U(III) or to a mixture of both.

Potassium dichromate is the most suitable reagent for sensitive results for all ranges of uranium including milligram levels. Ceric sulfate is also suitable but it is a stronger oxidant than dichromate and needs standardization. Also ferric sulfate and potassium permanganate are used.

4.B.ii. Reduction Procedure

Reduction procedure is preferred to oxidation procedure because oxidation step is eliminated. The most frequently used reductants are zinc amalgam, lead and chromous chloride in a hydrochloric acid media.

4.C. FLUORIMETRIC METHOD

This method is very sensitive in determination of very small quantities of uranium with a detection limit of about 10^{-11} g. Fluorimetry is widely used in analysis of rocks,

minerals, shales, soils and water (PI 75). The measurements
can be taken in a liquid media or after a fusion step. The
former procedure avoids high temperatures, but the latter is
more sensitive and is used widely. In fusion method uranium
is fused with sodium fluoride or sodium potassium carbonate
or both, and the resulting pellet is irradiated with ultra-
violet radiation to obtain a yellowish fluorescence. It is
important to take some parameters in to consideration; such
as the composition of flux, temperature and time of fusion,
cooling cycle, and time until measurements are taken. Also
pre-separation is necessary to avoid quenching, enhancing and
fluorescing of interfering elements (KO 62).

4.D. EMISSION SPECTROGRAPHY METHOD

The emission spectrum of uranium is easily recognized
from the great number of lines of low sensitivity. Low
volatility of uranium metal, because of the high boiling
point, also is a cause for the low sensitivity of the
spectrum. A comprehensive listing of spectral lines of
uranium gives 3554 emission and 2319 absorption lines (KO
62). Arc sources are suitable for the excitation of the ore
samples because they have high electrical resistance.

Flame excitation cannot be applied to atom because of
weak sensitivity of spectrum due to low volatility. The most
suitable condition for this method especially for refractory
samples is arc excitation combined with the analysis of the
spectrum. Spark excitation is also suitable for uranium
analysis (KO 62).

4.E. X-RAY METHOD

High atomic weight of uranium element compared with
others in alloys and in most ores allows this technique to be
applicable for uranium analysis. The methods usually applied
are absorption, fluorescence, Rayleigh scattering and absorp-

tion edge. Especially absorption edge spectrometry can be
used reliably for uranium in the presence of various elements.
Measurements are made by observing K, L and M levels in parti-
cular L(I) level (KO 62).

4.F. POLAROGRAPHIC METHOD

This method uses the reduction potential of U(VI) which
is easily reduced in electrolytes. Usually a pre-separation
of impurities increases the sensitivity especially when trace
amounts are present. Reduction potentials for U(VI) is in the
range of zero volts to -1.0 volt for strong mineral acid
solutions and for basic complexing solutions respectively.
The polarographic reduction of uranium may be done as follows.
U(VI) to U(V), U(V) to U(IV), U(IV) to U(III) and U(III) to U
amalgam. For quantitative analysis it is necessary to take
care of the reaction of U(V) because it gives a U(IV) and
U(VI) mixture. This can be controlled by pH adjustment or
complexing of uranium. The suitable instrumentation for
various matrices is a variable D.C. Voltage source and a
current measuring device usually in the microampere range (KO
62).

4.G. ISOTOPE DILUTION METHOD

This method depends on the addition of a known
quantity of a uranium isotope to the sample. After equilibra-
tion of sample and added uranium by chemical treatment and
mixing, uranium is concentrated using a separation procedure
and the ratio of the two isotopes is determined by mass
spectrometry. The separation need not be quantitative and
must only give a separated fraction of uranium with adequate
purity. This property is also useful in the presence of
impurities (KO 62).

4.H. RADIOCHEMICAL METHODS

The radioactive decay properties of the principle uranium isotopes have low activity and low energy of radiation, thus it is necessary to know well the isotopes and the activity they possess. The types of measurements are as follows (KO 62).

4.H.i. Alpha Spectrometry

Alpha particles have low mean free path and can be stopped by a thin sheet of paper. The alpha particles emitted from the natural isotopes fall in the energy range of 4 to 5 Mev. In this procedure a uranium isotope which is alpha emitter and which has a long half life is added in the sample. After equilibration is obtained between the sample and added uranium, uranium is separated from other elements present in the sample and is purified by extraction and/or ion exchange procedures and electroplated on a disc for alpha counting.

4.H.ii. Neutron Interaction Measurements

The two main isotopes found in natural uranium give different reactions under neutron irradiation. U(238) passes through a transmutation and yields ^{239}Pu as follows.

$$^{238}U + n \rightarrow {}^{239}U + \gamma$$
$$\downarrow \quad 23.5 \text{ m} \quad \beta^-$$
$$^{239}Np \xrightarrow[2.35 \text{ d}]{\beta^-} {}^{239}Pu$$
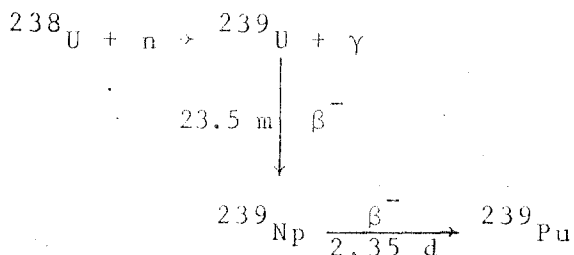
But U(235) fissions with neutrons. So, to determine uranium, activity of Np is measured or the fission fragments produced from the fission of U(235) are detected.

4.1. PHOTOMETRIC METHOD

Due to the fact that the colors of uranyl solutions usually remain in the visible range, photometry may be used in determination of uranium. For example uranyl nitrate has a maximum absorbance at 410 mμ. But uranyl salts usually have low molar absorption (about 1000 cm^{-1} $(moles/lt)^{-1}$) that it becomes necessary to use complexes with suitable chromogenic agents preceded by a separation process. The research done in the recent years led to chromogenic reagents with molar absorptivities between 70000-80000 which will give reliable results. The most sensitive chromogenic reagents in popular use are arsenazo and bromopadap (KO 62).

4.1.i. <u>UV-VIS Absorption Spectroscopy</u>

Determination of uranium in a solution, by using suitable chromogenic agents, especially organic, usually fall in the visible range of the electromagnetic spectrum. The electromagnetic spectrum consists of the following regions (MA 74).

1- Gamma ray region: Gamma radiation is emitted or absorbed as a result of transitions between nuclear energy levels. The wavelengths of gamma rays fall in the range from $3.9 . 10^{-10}$ to $4.7 . 10^{-13}$ m ($3.2.10^{-3}$. 2.66 MeV).

2- X-ray region: X ray radiation arises from transitions between the inner electronic levels of the atoms. The wavelength of X-rays is between 10^{-7} to 4.10^{-10} m ($1.25 . 10^{-5}$ - $3.12 . 10^{-3}$ MeV).

3- Ultraviolet-visible region: UV-VIS radiation is caused from the transitions between outer electronic levels of atoms and molecules. The range falls 4-780 nm (1 nm = 10^{-9} m) ($3.12.10^{-4}$ - $1.6.10^{-6}$ MeV).

4- Infrared region: Spectra of this region is due to the changes in vibrational energy levels of molecules. The wavelength range of this region is from 740 nm to 1 mm $(1.69.10^{-6} - 1.25.10^{-9}$ MeV).

5- Microwave region: The radiation that falls in this region is produced from the rotational energy changes of molecules and changes in the energies of unpaired electrons in an external magnetic field. The wavelength of this region is between 1 mm to 0.3 m $(1.25.10^{-9} - 4.16.10^{-12}$ MeV).

6- Radiofrequency region: The spectra of this region is obtained from the nuclear orientation in an external magnetic field. The wavelength range is between 0.3 m to 100 km $(4.16.10^{-12} - 1.25.10^{-17}$ MeV).

4.I.ii. Theory of UV-VIS Absorption Spectroscopy

The ultraviolet region of the electromagnetic spectrum covers the range from 4 nm to 380 nm, and the visible region from 380 nm to 780 nm. The energy of a molecule is composed of its electronic, vibrational and rotational energies. Electronic energy results from the transitions of electrons in a molecule or atom, vibrational energy is due to the vibrations of the constitutents of a molecule and rotational energy is due to rotation of the molecule. There are various vibrational and rotational energy levels for every electronic energy level. The absorption of the radiation causes a change in the energy level of the molecule, this is because of the electronic transitions of the molecule from the ground state to an excited state, therefore the molecule becomes excited. The energy emitted or absorbed during transitions are

$$E = E_i - E_j = h\gamma$$

where E_i is the energy of a higher level

        E_j is the energy of a lower level

        h   is the planck constant

        ν is the frequency.

Absorption spectroscopy of the inorganic compounds is not completely understood. The possible absorption processes are due to transitions within incompletely filled f orbitals, incompletely filled d orbitals of the metal ion and charge transfer transitions. The most important among the three is the charge transfer transitions (MA 74). Charge transfer occurs in the case of a complex if one component is electron donor and the other electron acceptor. During absorption, the electron passes from the orbital of the donor component to the empty orbital of the acceptor component and the complex therefore becomes excited.

4.I.iii. Mathematical Statement Used in the Measurements of UV-VIS Absorption Spectroscopy

The quantitative application of the UV-VIS absorption spectroscopy lies in Beer-Lambert law as follows. The law states that there is a relationship between the intensity of a monochromatic beam incident on a liquid, the intensity of the same beam that traversed the liquid and absorbing material on the path of the beam. Mathematically it is given as

$$I = I_o e^{-acl}, \text{ where}$$

I_o is the intensity of the incident beam

I intensity of the traversing beam

a absorptivity cm^{-1} $(g/lt)^{-1}$

C molar concentration g/lt

l path length (cm)

If the absorbing medium is completely traversed $I = I_c$ and another quantity is introduced as

$$T = \frac{I_c}{I_o} \qquad \text{or more precisly,}$$

$$T = \frac{I_c}{I_o} = e^{-acl} \qquad \text{where T is the transmittance}$$

The relationship between T and C is inconvenient for most purposes. Then a more suitable quantity, absorbance A, which is the log T with the negative sign is used

$$A = -\log T = acl$$

Another representation is

$$A = \varepsilon Cl$$

in this case l has units of cm, C(moles/lt) and ε is called molar absorptivity and has the units cm^{-1} $(moles/lt)^{-1}$ (MA 74).

4.I.iv. Instrumentation for the UV-VIS Region

Usually, the radiation source used for the UV region is hydrogen arc lamp and for the VIS region it is tungsten lamp. Monochromators are used to isolate one wavelength of radiation. The components of a monochromator are entrance slit, collimator, dispersion prism, focusing lens and exit slit. For detection and measurements photomultiplier tubes and photographic detectors are used. The sample cells are placed behind the monochromator.

For the UV-VIS spectrum double beam spectrophotometers with monochromators of 1 nm resolution are used. The sample cells are glass for VIS and quartz for the UV range. The path

length of the cells is usually 1 cm but could be up to 10 cm. Some of the solvents used, which must be transparent in this range are water, ethanol, benzene and chloroform (MA 74).

CHAPTER 5
FROTH FLOTATION

The purpose of this chapter is to give a description about the theory of flotation, the main steps of a flotation operation and the types of reagents used and their importance on a flotation operation.

5.A. INTRODUCTION

The production of uranium from its ores mainly follows a leaching, separation and reduction to metal or fluorination of uranium compound. The primary step in production is leach-ing, acid or alkali leaching depending on the nature of the ore. Uranium is found in nature as considerably low grade ore compared to other minerals. The grade of ores accepted as economic, range between 0.05-3%. Therefore, to lower the reagent losses the application of mineral dressing processes is necessary. A suitable process is chosen according to the minerals the ore contains. The sediments of Black Sea show a distribution of very small particles. The sediments are rich in organic matter and clay minerals (DE 77) and the bulk of uranium is bound to the organic matter (DE 77). Therefore, to obtain a concentrate in which uranium is dominant, flota-tion seems to be a suitable process among other processes as described in Chapter 3.

Flotation is a separation process. Flotation appears

under the generic name of Adsorptive Bubble Separation Methods (LE 68) or Adsubble methods. The classification in a suitable scheme is given in Fig 5.1.

Today widely used application of the flotation appears in ore flotation. The products of a flotation process are concentrate and tailing. Concentrate is the yield containing the valuable part and tailing the worthless part. The flotation medium is usually water where the particles are suspended. The ore has to be ground and crushed to a suitable size that the minerals which are to be concentrated must be of only valuable or worthless substance. This step is called liberation step. The separation is obtained by producing a water-repellant coating on the mineral particles which must also be suitable in the adhesion to gas bubbles. As a result a froth is obtained which differs in composition from the pulp (GA 57).

5.B. THE PHASES IN FLOTATION SYSTEMS

5.B.i. The Gaseous Phase

Gaseous phase is important in a flotation operation because it provides the adherence of particles to the bubbles and makes possible the flotation of the particles. The usually employed material for the gaseous phase is air. The other materials used are steam, nitrogen, sulphurdioxide, oxygen and hydrogen sulphide (AT 74).

5.B.ii. The Liquid Phase

The liquid phase of a flotation operation is usually water. H_2O is used extensively because it is cheap, available and found most suitable for the flotation operation (AT 74).

ADSORPTIVE BUBBLE SEPARATION METHODS

Foam Separation

Foam
Fractionation

(Froth) Flotation

Ore
flotation

Macro
flotation

Micro
flotation

Precipitate
flotation

Ion
flotation

Molecular
flotation

Nonfoaming Adsorptive
Bubble Separation

Solvent
sublation

Bubble
fractionation

Absorbing
colloid
flotation
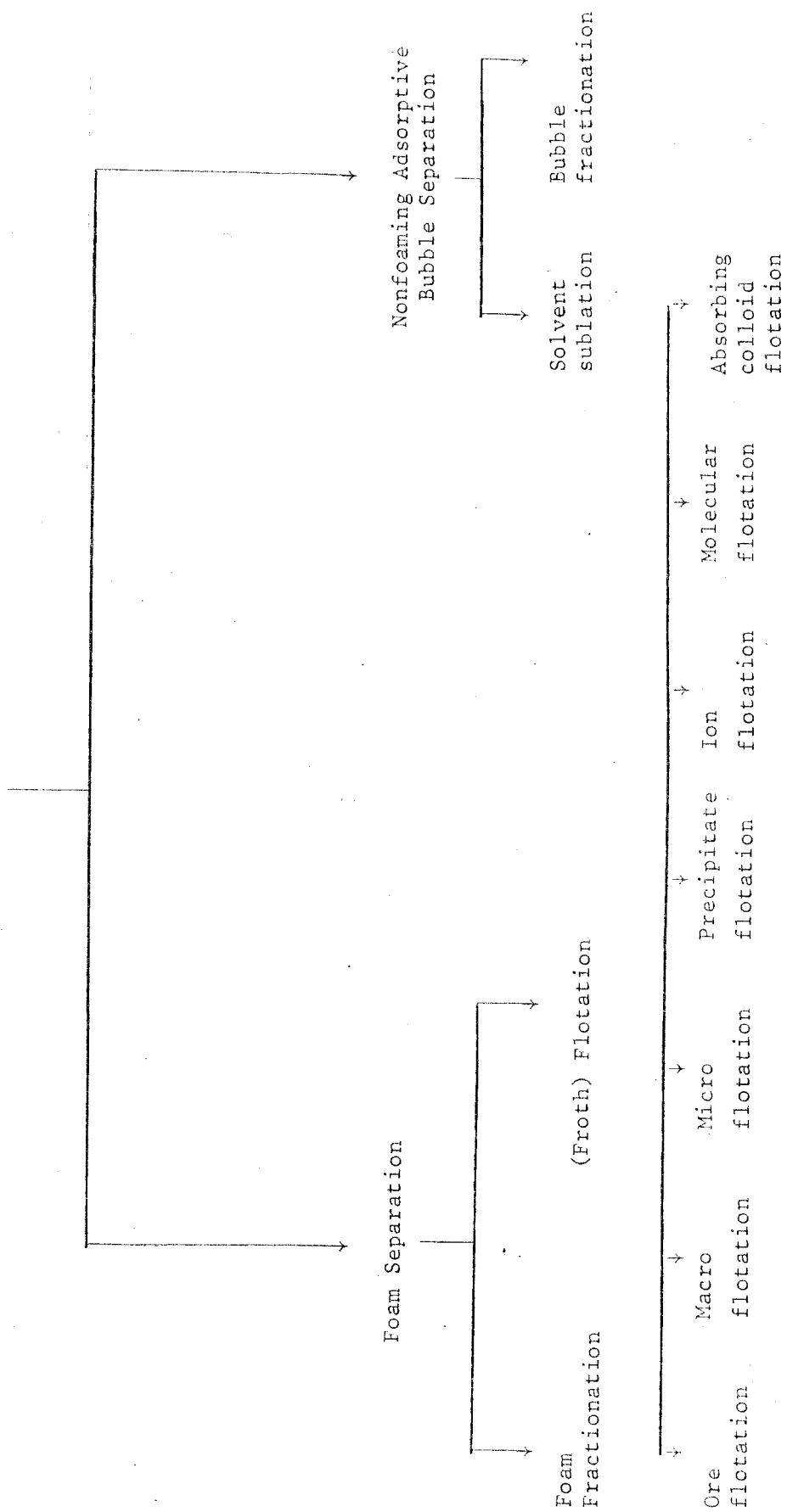
Fig.5.1- The scheme of adsorptive bubble separation methods (LE 68).

5.B.iii. The Solid Phase

Since solid particles are floated, solids and their surface properties are important. The usually encountered crystal types of solids are as follows (GA 57).

1- Atomic crystals: Atomic crystals are found among the solidified noble gases.

2- Molecular crystals: Many compounds from the field of organic chemistry and inorganic chemistry are of this type, e.g. iodine, nitrogen, methane.

3- Filament and sheet crystals: The most representative examples of filament crystals are selenium, tellurium, sulphur.

4- Diamantine crystals: These crystals are typified by the diamond.

5- Simple ionic crystals: Common salt is of this group.

6- Fiber, layer and framework ionic crystals: Feldspar, kaolin and gibbsite.

7- Metallic crystals: Metals form this type of crystals (GA 57).

5.C. THE PHYSICAL CHEMISTRY OF FLOTATION

In every flotation operation three phases namely gas, liquid and solid are in contact. To clarify the properties of a flotation operation, the physical and chemical properties of the interface of these three phases need to be studied.

Most of the flotation reagents, organic or inorganic,

are electrolytes i.e. they form a solution containing negati-
vely and positively charged ions. In addition to during opera-
tion some of the solids of the pulp pass the solution,
forming charged ions of different charges. From the surface
of a solid in water. electrically charged particles pass   to
the liquid phase until they reach an equilibrium. Ions
diffusing from the solid to the liquid or vice versa cause
the surface of the solid to have an electrical charge of
specified sign and quantity (AT 74). Those ions that specify
the electrical charge of the surface are called potential
determining ions. These ions of opposite signs that balance the
electrical charge of the surface are called potential deter-
mining ions. These ions of opposite signs balance the elec-
trical charge of the solid surface and are called counter
ions. The concentration of counter ions decreases as the
distance from the surface increases and reaches to the con-
centration of the solution. When the chemical equilibrium is
reached the charge on the solid surface reaches to an
equilibrium with the dispersed charge, that is the potential
of the surface of the mineral becomes zero which resembles
the plates of a capacitor and is called the electrical double
layer (AT 74).

5.C.i. Relationship Between the Composition of the Surface
        Layer of a Solution and of the Bulk of the Solution

Willard Gibbs established a relationship between the
composition of the surface layer of a solution and of the
bulk of the solution (GA 57). This relationship is named
Gibbs Absorption equation and can be written as.

$$\Gamma = - \frac{C}{RT} \frac{\partial \gamma}{\partial C} \qquad \text{where}$$

Γ is the excess solute

C   concentration

R   Gas constant

T   Absolute temperature

γ   Surface tension

For a pure liquid Γ is zero. If the concentration of a material in a solution diminishes towards the surface one obtains a negative Γ as it is in the case of anorganic salts.

If the concentration of a material increases close to the surface Γ takes a positive value as it is in the case of organic compounds (AT 74).

5.C.ii. The Angle Between Three Phases in Contact

In a flotation operation, when two phases such as gas-liquid or solid-liquid come into contact, form a two dimensional surface, while the contact of three phases such as gas, liquid and solid, form a one dimensional line. In the case of gas, solid and liquid phases the contact angle is as shown in Fig 5.2. (AT 74). In this figure γ_{GL} is gas-liquid interface surface tension, γ_{LS} is liquid-solid interface surface tension, γ_{SG} solid-gas interface surface tension. At equilibrium the summation of the three surface tensions equals zero.

$$\gamma_{GL} + \gamma_{LS} + \gamma_{SG} = 0$$

$$\gamma_{GL} Cos\theta = \gamma_{SG} - \gamma_{LS}$$

$$Cos\theta = \frac{\gamma_{SG} - \gamma_{LS}}{\gamma_{GL}}$$

The relation $\gamma_{SG} - \gamma_{LS} \leq \gamma_{GL}$ represents the floatability of the solid, while

$$\gamma_{SG} - \gamma_{LS} > \gamma_{GL}$$

represents depression of the solid (AT 74).

5.D. FLOTATION REAGENTS

Flotation agents are substances added to the ore or pulp to make possible or to facilitate the treatment. Flotation reagents according to their importance are named collectors, modifiers and frothers.
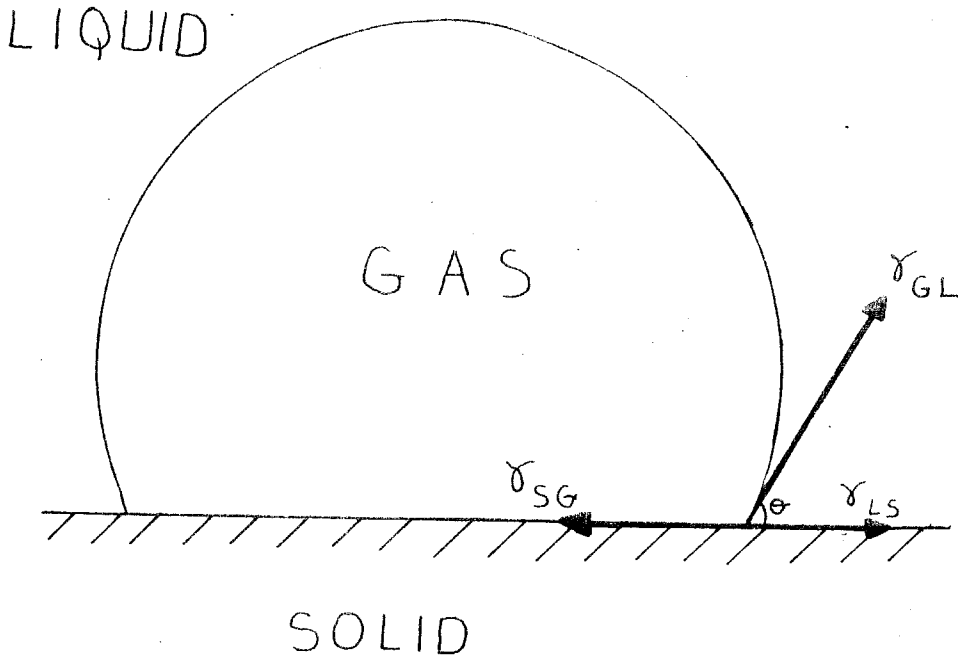
Fig.5.2- Bubble attached to solid in liquid phase (AT 74).

5.D.i. Collectors

Collection is performed for the purpose of producing selective water repellant coatings on the mineral particles which are to be separated from the pulp in order that gas bubbles may cling to these particles. Organic acids, bases and salts furnish most flotation collectors. Collectors are divided into two broad groups (GA 57).

a) Anionic Collectors

These are characterized by an organic acid group. They include carboxylates, acid alkyl sulfates and sulfonates, sulfhydryl compounds, mercaptans, thiocarbonates, thioureas, dithrocarbonates and dithiophosphates.

i) Oxyhydryl Anionic Collectors

1- Carboxylates: These are the metallic salts of the fatty acids. General formula is

$$R-\underset{\underset{O}{\|}}{C}-O \ldots H$$
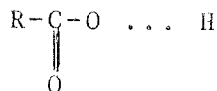
2- Acid Alkyl Sulfates: They are represented as

$$R-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O \ldots H$$
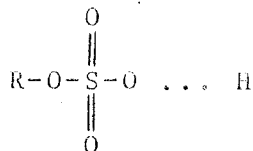
There are the salts of alkyl sulphuric acids. They could be obtained from the reaction of sulphuric acid and alcohols, olefins with sulphuric acid, or using sulphating agents instead of sulphuric acid.

ii) <u>Sulfhydryl Anionic Collectors</u>

1- Thiols: General formula is R-S ... H. Thiols are organic compounds containing the -SH group in combination with an organic radical.

2- Thiocarbonates: General formula is

R-O-C-S ... H (or M)
     ‖
     S
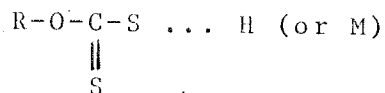
They are widely known as xanthates and are useful for the flotation of the heavy and precious metals (TA 45).

3- Thiocarbonates: General formula is (TA 45)

        R
        |
R-N-C-S ... H
    ‖
    S
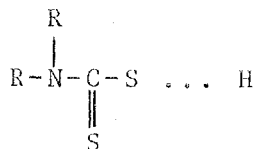
4- Thiophosphates: General formula is

R
 \
  O   S
   \ //
    P - S ... H (or M)
   /
R-O
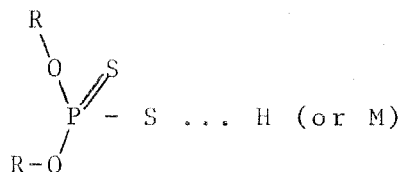
The products with phenols and alcohols are the ones in common use. Here R denotes alkyl or aryl radical and M an alkali metal or ammonium ion.

b) <u>Cationic Collectors</u>

General formula is

$$R'' \diagdown \diagup R'$$
$$\diagup N \quad \ldots \quad OH$$
$$R'' \quad | \quad$$
$$R$$
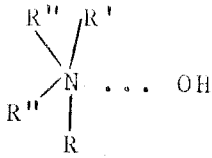
These are ionizable organic compounds in which the ion that carries the hydrocarbon and reactive groups is the cation. Primary, secondary, tertiary and quaternary amines, alkyl amines, aryl amines and alkyl aryl amines are of this group (CA 57).

5.D.ii. Modifiers

Modifiers or regulators are used extensively in flotation to modify the action of the collector either by intensifying or reducing its water repellant effect on the mineral surface. These are classified as activators, depressants and regulating and dispersing agents(1).

a) Activators

Chemicals of this group are used to effect the flotation of certain minerals that are normally difficult or impossible to float with collectors and frothers alone. Some of the activating agents are copper sulphate, lead nitrate, lead acetate and sodium sulphide.

b) Depressants

Depressing agents assist in the separation of one mineral from another, when floatabilities of two minerals to be separated are quite similar. Some of the depressing agents are glue, gelatin, tannin, sodium silicate and ferrocyanide(1).

c) Regulating and Dispersing Agents

The function of the reagents included in this group is to control alkalinity or acidity and also to counteract the interfering effect of slimes, colloids and soluble salts. Sulphuric acid, phosphates, lime, soda ash are some samples of this group(1).

5.D.iii. Frothers

Production of a persistent froth of desired selectivity is very important. Frothing involves the introduction of small air bubbles in to the flotation pulp and collection of the unbroken mineral carrying bubbles on the pulp surface. This is accomplished by the introduction of a frothing agent or frother in to the ore pulp.

An effective frothing agent must be capable of passing readily into the interface between liquid and gaseous phases attached to the solid so that the solid will adhere to the bubble and be raised towards the surface (GA 57). Most widely used frothers are heteropolar i.e. which contains a polar part (water avid) and nonpolar part (water repellent). At an air water interface such frothers are oriented with the polar group toward the water and the nonpolar toward the air. The most effective frothers include in their composition one of the following groups (WI 79).

Hydroxyl - OH

Carboxyl - $\overset{\displaystyle O}{\overset{\|}{C}}$ - OH

Carbonyl $=C=O$

Amino group $-NH_2$

Sulpho group $- OSO_2OH$

Commonly used frothers are pine oil, cresylic acid and certain synthetic alcohols (GA 57).

CHAPTER 6

EXPERIMENTAL PROCEDURE

In the first half of this chapter uranium analysis is discussed. In the analysis, the procedure suggested in the literature was somewhat modified because the uranium content of the sediments was lower than expected and it wasn't possible to determine the concentration of uranium in the sediments by direct application of the procedure. In the latter part of the chapter flotation experiments that were performed are discussed. The discussion of the results of the experiments are given in Chapter 7.

6.A. PROPERTIES AND WATER CONTENT OF THE SEDIMENTS

The sediments used for the analytical and flotation studies are from a sample taken from the following location in Black Sea.

Core No	: 65A
Longitude	: 40°
Latitude	: $41^\circ 31'$
Depth	: 1880 m
Date	: October 4 1978

The core was taken by a Turkish naval force ship.

After drying, the mud hardens and takes a grey colour similar to cement. The water content of the core mud was measured at $105^{\circ}C$ with four samples which were taken before mixing the mud homogenously. The samples were dried at $105^{\circ}C$. in an air oven, from Baird and Tatlock LTD. Essex England, until the samples reached a constant weight*.

6.B. COMBUSTION EXPERIMENTS OF THE SEDIMENT

The mud contains organic matter (DE 77) and since uranium is mostly bound to the organic matter, experiments for combustion were carried out in order to obtain a sediment rich in uranium content from the original one. The experiments were performed in an electrically heated muffle furnace from Blue M Electric Company, Blue Island Illinois USA Part No C-3946-Q. The experiments were carried out on samples dried at $105^{\circ}C$. The temperatures applied were 400-600-800 and $1000^{\circ}C$. The results are shown on Table 6.1.

TABLE 6.1- RESULTS FOR COMBUSTION OF SEDIMENTS

Experiment No	Temperature $^{\circ}C$	Time Minutes	Weight Before Combustion(gr)	Weight After Combustion(gr)	Weight Loss %
1	400	240	83.2553	81.3013	2.35
2	600	210	10.1046	9.9105	1.92
3	800	240	32.2036	30.9171	4.00
4	1000	120	108.6878	102.7155	5.49

---

* The results of the drying experiments varied between 12.7%-25.9% of water content.

6.C. COMPARISON OF VARIOUS ANALYSIS METHODS

For the qualitative and quantitative analysis of elements of trace amounts most commonly used methods are activation analysis, fluorimetry and spectrophotometry. But some other methods or combinations of them could be used such as coprecipitation and fluorimetry, anion exchange and spectrophotometry, colloid flotation and spectrofluorimetry etc. (RI 75). Since the element that is needed for determination and estimation purposes is in a mixture of elements which affects the results, methods such as gravimetry, titrimetry etc., are not suited to obtain reliable results when trace amounts of element is present. However activation analysis, fluorimetry, spectrophotometry and even isotope dilution could be used in the presence of various elements for the determination of trace amounts.

Activation analysis needs a high neutron flux of about $10^{13}-10^{15}$ neutrons/sec. and analysis of the results with the aid of a computer. Activation analysis is reliable but was not attempted in this study.

Fluorimetry is a widely used method in determination of trace elements. For satisfactory results it could need a pre-separation process.

Spectrophotometric method is also one of the more sensitive methods. Until recently it had some drawbacks that have been overcome as a result of investigations as discussed below. Since a solution is necessary for the measurements in the case of solid samples it was difficult to obtain a complete decomposition and it usually required alternative treatments with strong acids although usually a residue remained. But this problem is solved by using a teflon crucible placed in a

steel bomb (BE 68). Another disadvantage is a suitable chromogenic agent, usually organic, to enhance the colour to take the measurements. For uranium this problem is solved with bromo padap (JO 71) which has a molar absorptivity about 80 000 and with this it is possible to determine trace amounts of uranium. Thus this makes spectrophotometric method comparable with fluorometric method that both of them are versatile, practical and applicable in laboratories and do not need very complex instruments.

Usual procedure for fluorimetry is to mix the unknown sample with about 10 fold sodium potassium carbonate mixture and activate the compound and then measure the fluorescence. But for sensitivity a separation of interfering elements is needed. Up to this point this method is paralel to spectro-photometry method. After separation, fusion is applied at elevated temperatures and irradiated with ultraviolet radiation and the fluorescence is measured by a fluorescencemeter. But for reproducible results it is necessary to take various parameters as described in 4.C, in to consideration.

In spectrophotometric method after separation the chromogenic reagent is added and the resulting colour is measured with a spectrophotometer. Since both methods are equally sensitive spectrophotometric method was chosen for analytical purposes. The analytical procedure was based on two recent works (JO 71, PA 74).

6.D. INSTRUMENTS AND REAGENTS

6.D.i. Instruments

The instruments that were used were acid digestion bomb, spectrophotometer and quantitative glassware such as measuring cylinder, pipets etc that are generally used in

quantitative analytical laboratories. The stainless steel digestion bomb of 25 ml and Teflon cup with cover is from Parr Instrument Co. The spectrophotometer used in experiments is 635 D Varian Techtron spectrophotometer.

6.D.ii. Reagents

The reagents used in these analytical experiments are the yield of a detailed study on determination of uranium. These are complexing solution, dilute complexing solution, buffer solution, bromopadap solution, TOPO solution, standard uranium solution and silica fluoroboric acid solution. These solutions are prepared as follows.

i) Complexing Solution

This is prepared with 1,2 cyclohexylene dinitrilotetra acetic acid (CyDTA) (Aldrich) 25 gr, sodium fluoride 5 g, sulphosalicylic acid 65 g suspended in 800 ml of water and neutralized to pH 7.85 with 40% sodium hydroxide and diluted to 1 lt (FL 63). This solution complexes Th, Be, Al.

ii) Dilute Complexing Solution

An aliquot of complexing solution is diluted 1:1 volumetrically with water and set to pH 8.35 with 40% sodium hydroxide (JO 71).

iii) Buffer Solution

149 g of triethanolamine is dissolved in 800 ml of water and neutralized to required pH with perchloric acid and allowed to stand overnight and readjusted to pH 8.35 with perchloric acid and diluted to 1.1. (FL 63).

iv) Bromo Padap Solution

2-(5-bromo-2-pyridylazo)-5-diethylaminophenol. Uranyl bromopadap complex has a molar absorptivity of 74 000 at 578 nm at pH 7.6 (JO 71). 0.05 g Bromo Padap (Aldrich) is dissolved in 100 ml of reagent grade ethanol to obtain 0.05% bromo padap solution.

v) TOPO Solution

19.3 g. of tri-n-octylphosphine oxide (KODAK) is dissolved in cyclohexane and diluted to 500 ml to obtain 0.1M solution of TOPO (JO 71). TOPO could extract more than 99% of uranium (FL 70) and 0,00025 M TOPO is sufficient for the extraction of several milligrams of uranium (BA 64).

vi) Standard Uranium Solution

To prepare the solution uranium metal is used. Properties of the plate are; weight 1.4140 g, impurities Al less than 0.01%, Fe less than 0.02%, Purity 99.97%. 0.1791 g. uranium metal is dissolved in concentrated nitric acid and diluted to 100 ml with water.

vii) Silicafluoroboric acid Solution

The silicondioxide required for this solution was obtained from Paşabahçe glass and bottle factory, because pure silicon dioxide was not available. The preparation is as follows. 0.107 g of 97% silicon dioxide in the form of quartz is dissolved with hydrofluoric acid of 3.6 ml. 1 ml of aqua regia is added with 1.3 g boric acid and diluted to 100 ml with water (PA 74).

6.E. SPECTROPHOTOMETRIC DETERMINATION OF URANIUM IN BLACK SEA SEDIMENTS WITH BROMO PADAP

6.E.i. Detection and Determination of Uranium in Standard Solutions

Primary studies were carried out to become acquainted with the procedure. Various standard solutions of uranium were prepared and the following solutions were added with mixing, 2.0 ml of complexing solution, 2.0 ml of pH 7.85 buffer, the volume of 1M NaOH for neutralization if necessary, 100 ml of ethanol and 2.0 ml of 0.05% bromo-Padap respectively then mixed and diluted to 25 ml. After 40 minutes the colours were measured against a reagent blank at 578 nm (JO 71). The results are shown in Table 6.2.

TABLE 6.2- CONCENTRATIONS OF STANDARD URANIUM SOLUTIONS and RELATED SPECTROPHOTOMETER READINGS

Sample No	Concentration μgU / ml	Absorbance
1	10	8.36
2	4	1.21
3	1	0.256
4	0	0

6.E.ii. Primary Analysis For Determination of Uranium in Sediments Using 5.0 ml TOPO Solution

A calibration graph was prepared to use in the calculation of the uranium content of the sediment. For this graph aliquots were taken from the main standard uranium solution and direct method (PA 74) was

applied on these aliquots. The results are shown in Table 6.3 and on Fig.6.1. Least squares method, presented in detail in Appendix I, was applied for the calibration graph on the Fig.6.1.

TABLE 6.3- CALIBRATION GRAPH VALUES PREPARED BY DIRECT METHOD (PA 74)

Sample	1	2	3	4	5	6	7	8
Concentration μgU / ml	1.28	0.96	0.8	0.64	0.32	0.16	0.016	0
Absorbance	0.344	0.273	0.249	0.185	0.10	0.048	0.008	0

The determination of uranium in sediments was carried out using direct method (PA 74). To reduce or to observe if whether there would be any errors, standards were added to the sediment and direct method (PA 74) was applied to the sediment and the sediment plus the standard. The results are summarized in Table 6.5. The amounts of the decomposition step were reduced to the half of the actual values because this caused the acids added to overflow.

TABLE 6.4- ANALYSIS OF SEDIMENTS USING DIRECT METHOD (PA 74)

Sample	A	B	C*
Composition	80 μgU + 0.1 g sediment	1 μgU + 0.1 g sediment	Blank
Absorbance	0.333	0.015	0.064

* C was measured versus ethanol.

Since the absorbance readings obtained from the spectrophotometer showed very low values, it was decided that the reason for this was sodium fluoride because it was predicted that (JO 71) excess sodium fluoride depresses
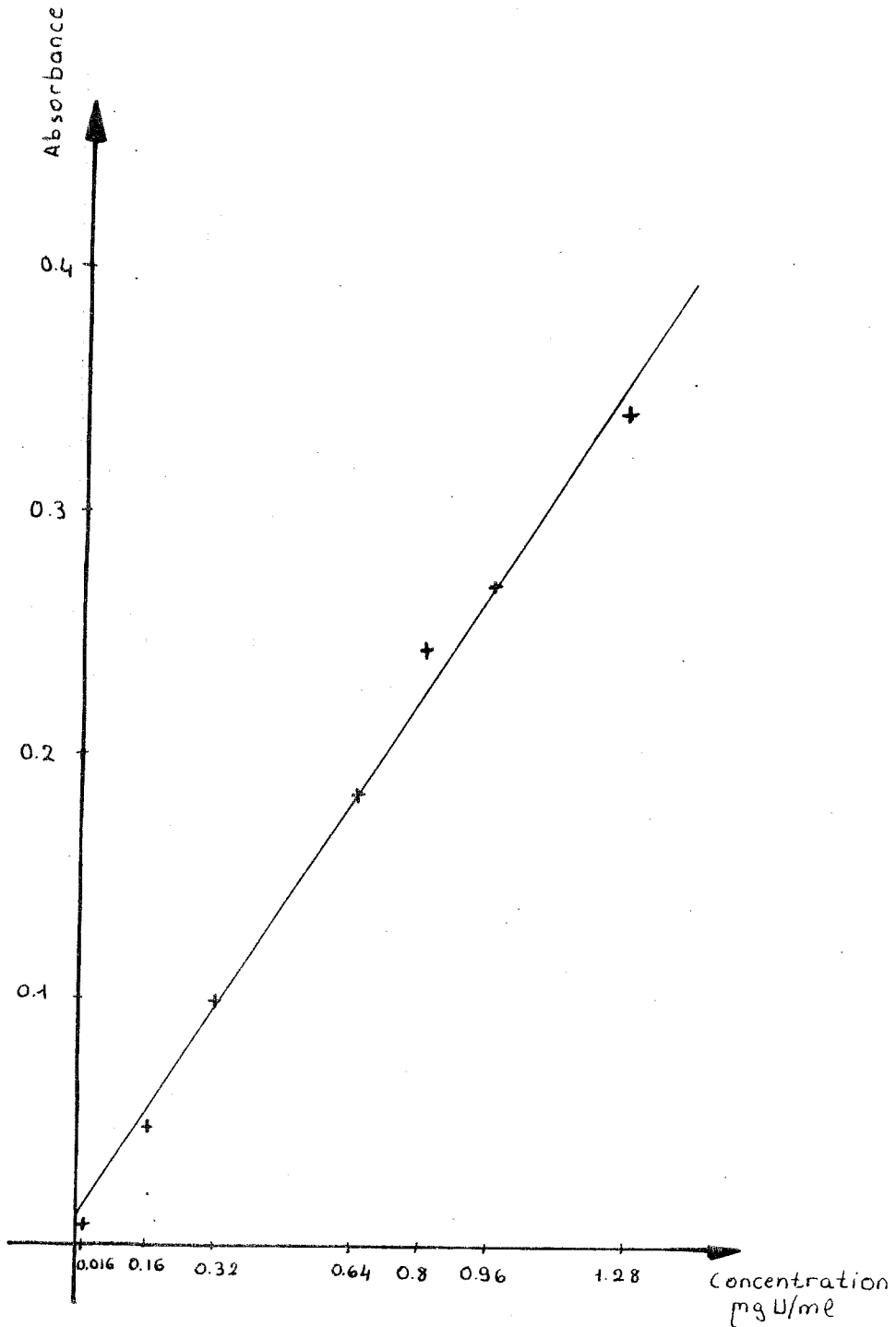
Fig.6.1- Calibration curve prepared from standard uranium solutions using direct method as described in (PA 74)

(Standard deviation of this fit is found to be ~ 0.0122)

uranium. Sodium fluoride is used to complex Zr and Th to
prevent their extraction with TOPO (Since complexing solution
includes sodium fluoride). The experiment was repeated three
times with the results shown in Table 6.5. The procedure is
as follows. 0.1 g sediment or standard with 0.1 g sediment
was passed from the decomposition procedure. The decomposed
sample was transferred to a beaker containing 0.65 g of boric
acid, diluted to 50 ml. and heated in order to dissolve the
fluoride precipitate and transferred to a 100-ml volumetric
flask and diluted to full volume with water. 5 ml of this solution
was transferred in to a 50 ml volumetric flask. 4.0 ml of
complexing solution was added and was left to stand for 15
minutes. Then 2.0 ml of freshly prepared 5% ascorbic acid
solution was added and mixed and extraction was applied with
the addition of 5.0 ml of 0.1 M TOPO solution (NaF step here
was omitted). Then 2.0 ml of organic phase was transferred in
to 25 ml volumetric flask and 1.0 ml of dilute complexing
solution, 4.0 ml of 0.05% bromo PADAP and 1.0 ml of pH 8.35
buffer were added respectively and mixed after each addition.
After 10 minutes 16.0 ml of ethanol was added and diluted to
volume with water and the colour was measured against a
reagent blank carried out through the same procedure.

TABLE 6.5- ANALYSIS OF SEDIMENT WITHOUT NaF ADDITION

Sample		I	II	III	IV	A
Composition		5 µgU	0.1 gr Sediment	5 µgU+0.1g Sediment	Blank	
Absorbance	First experiment	0.015	0.003	0.017	0.062	0.006
	Second repeat	0.023	0.006	0.023	0.063	0.008
	Third repeat	0.020	0.004	0.026	0.064	0.011

The colours of the samples were measured in the spectrophotometer versus the blank which didn't contain any uranium in it. Blank was also measured versus ethanol because it was the main solution to see if the composition of the blank varies considerably from one experiment to another. To ascertain the values of column II, on a separate reading, number III was measured versus number I instead of blank and the results were obtained as could be seen on column A.

Some previous studies performed on Black sea sediments (2,3) showed that the sediments contain Zr and Th, which cause interferences in the spectrophotometric determination of uranium. Another study was carried out by exact application of the direct method (PA 74) to compare the results with the experiments shown in Table 6.5. The results are shown in Table 6.6.

TABLE 6.6- ANALYSIS OF SEDIMENT BY DIRECT METHOD (PA 74)

Sample		A	B	C	D	C-A
Composition		7.16 µgU	0.1 g Sediment	7.16 µgU + 0.1 g Sediment	Blank	
Absorbance	First experiment	-0.000	0.000	0.000	0.061	0.008
	Second repeat	0.023	0.001	0.028	0.062	0.001

The silicon dioxide employed to prepare silicafluoroboric acid to use in blank solutions was taken from Paşabahçe factory, and it was decided to test whether it contained uranium in ppm range. The silicon dioxide was examined in an experiment versus distilled water. The results of this experiment are shown in Table 6.7.

TABLE 6.7- ANALYSIS OF SILICONDIOXIDE

Sample	Blank Prepared With Distilled Water	Blank Prepared With Silicafluoroboric Acid
Absorbance	0.060	0.065

Source: Paşabahçe fac.

6.E.iii. The Second Step In Analysis For Determination of Uranium in Sediments Using 3.0 ml TOPO Solution

The absorbance values obtained from the spectrophotometer were considerably low so that it was not possible to reach the desired sensitivity. A solution to this problem was to increase the amount of the ore. The decomposition bomb has a volume of 25 ml and it is not possible to decompose samples to less than 0.2 gr. Therefore, a decomposition procedure similar to the one described in (JO 71) was applied using the teflon cup only. Another solution to increase the sensitivity appeared by decreasing the amount of TOPO solution from 5.0 ml to 3.0 ml because 2.0 ml was needed for the measurements and 3.0 ml of solution leads to a more concentrated extract in comparison with the amount 5.0 ml case. Therefore at this step the amount of TOPO solution was taken as 3.0 ml. besides this amount is also suitable for the extraction of several milligrams of uranium (BA 64). The results of the calibration curve prepared with 3.0 ml of TOPO is shown in Table 6.8. The values are marked on Fig.6.2. and least squares method (Shown in Appendix I) was applied to the experimental results. The graph gives a linear line which shows that Beer's law is obeyed.
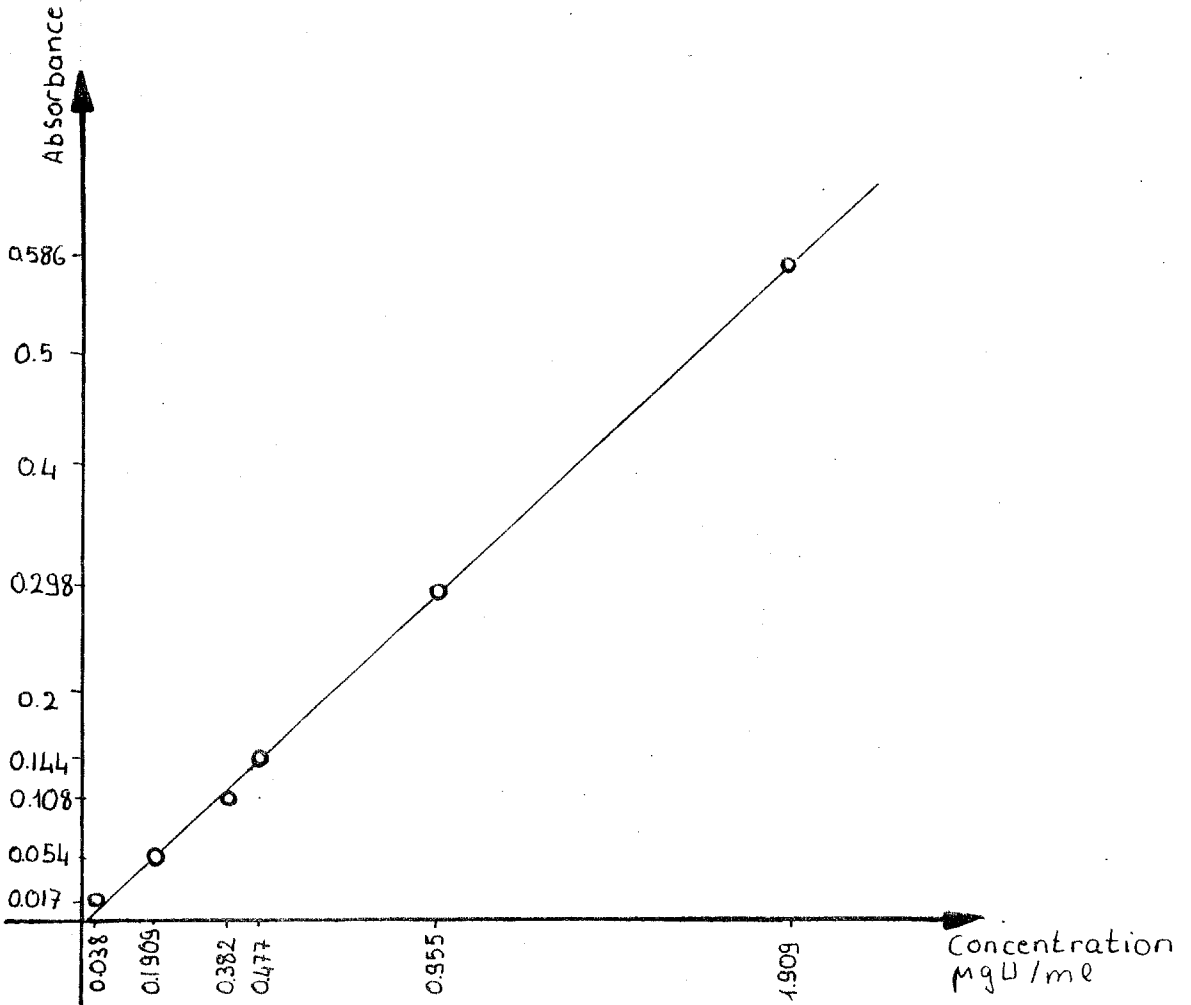
Fig.6.2- Calibration curve prepared using 3 ml of TOPO solution for extraction. (Standard deviation of this fit is found to be 0.00601).

TABLE 6.8- RESULTS OF CALIBRATION GRAPH OBTAINED BY 3.0 ml OF
TOPO SOLUTION

Standards	A	B	C	D	E	F
Concentration of final solution μgU/ml	1.909	0.955	0.477	0.38	0.1909	0.038
Absorbance	0.586	0.298	0.144	0.108	0.054	0.017

The second step in the determination of uranium content of the sediments was carried out as follows: 2.00 gr of sediment was decomposed in the teflon cup. The decomposition was performed in six steps and a total of about 30 ml of nitric acid and 3.6 ml of hydrofluoric acid were used. In the first five steps an aliquot of nitric acid (about 5 ml) was added and evaporated to dryness. At the sixth step the remaining nitric acid and 3.6 ml of hydrofluoric acid were added and again evaporated to dryness. The residue was then dissolved in hot water and diluted to about 20 ml with water. Concentrated solutions containing 2.0 g sodium fluoride and 2.0 gr ascorbic acid were added respectively and mixed after each addition. Then 3.0 ml of 0.1 M TOPO solution was added and extracted for 1 m. 2.0 ml of organic phase was transferred in to a volumetric flask. 1.0 ml of dilute complexing solution, 4.0 ml of 0.05% bromo PADAP, and 1.0 ml of pH 8.35 buffer were added respectively. After 10 minutes of waiting period (for the colour to develop) 16.0 ml of ethanol was added and diluted to volume with water. The results are shown in Table 6.9.

TABLE 6.9- ANALYSIS OF SEDIMENT TAKING 2.0 gr FOR DECOMPOSITION

Sample		Unknown
Absorbance	First Experiment	0.030
	Second Repeat.	0.028

The amount of uranium in the sediment is calculated as follows. For the first experiment:

From Fig.6.2. 0.030 gives 0.1 µg/ml.

$$\text{Amount of Uranium} = \frac{0.1 \ \mu g/ml \ \times \ 25 \ ml \ \times \ 3 \ ml}{2 \ ml}$$

$$= 3.75 \ \mu gU/2.00 \ gr$$

$$= 1.87 \ \mu gU/1.00 \ gr = 1.87 \ ppm.$$

In order to have reliance on this procedure it was examined with the decomposition procedure as described in (PA 74). In order to facilitate the measurements a standard of 71.6 µgU was added on to 0.1 g of sediment and 5.0 ml of TOPO was used at the extraction step. The results are shown in Table 6.10.

TABLE 6.10- COMPARISON OF THE DECOMPOSITION PROCEDURES

Sample	Unknown A	Unknown B
Procedure	Decomposition in the open teflon cup	(PA 74)
Absorbance	0.156 (33 µgU)	0.244 (54.5 µgU)

Table 6.10 indicates that the decomposition procedure as described in (PA 74) was more reliable.

6.E.iv. <u>Final Form of Analysis For Determination of Uranium In Sediments</u>

The amount of sediment was restricted to 0.2 gr (using a new teflon cup) and standard addition method was used to determine the uranium content of the sediments. The concentration of uranium is found by a graphical solution in standard addition method. Standards were added to the 0.2 gr sediment and passed from the decomposition procedure (PA 74) closed tightly in the steel bomb. The absorbance values (obtained as described below) were marked on a coordinate system and the line where it intersects with negative x-axis gives the uranium content of 0.2 gr sediment. The result are shown in Table 6.11 and the values are marked on Fig.6.3.

TABLE 6.11- RESULTS OF THE ANALYSIS OF THE SEDIMENT WITH STANDARD ADDITION METHOD

Sample	A	B	C	D	E	F
Composition	Blank + 0.2 gr Sediment	$1.432\mu gU$ + 0.2 g Sediment	$4.29\mu gU$ + 0.2 g Sediment	$7.16\mu gU$ + 0.2 g Sediment	$11.45\mu gU$ + 0.2 g Sediment	$14.32\mu gU$ + 0.2 g Sediment
Absorbance	0.009	0.029	0.054	0.062	0.112	0.132

A new calibration curve was prepared by applying the decomposition procedure (PA 74) to the standard solutions and aplying the spectrophotometric method (JO 71) to the decomposed sample. The results for the calibration curve are shown in Table 6.12 and marked on Fig.6.4.
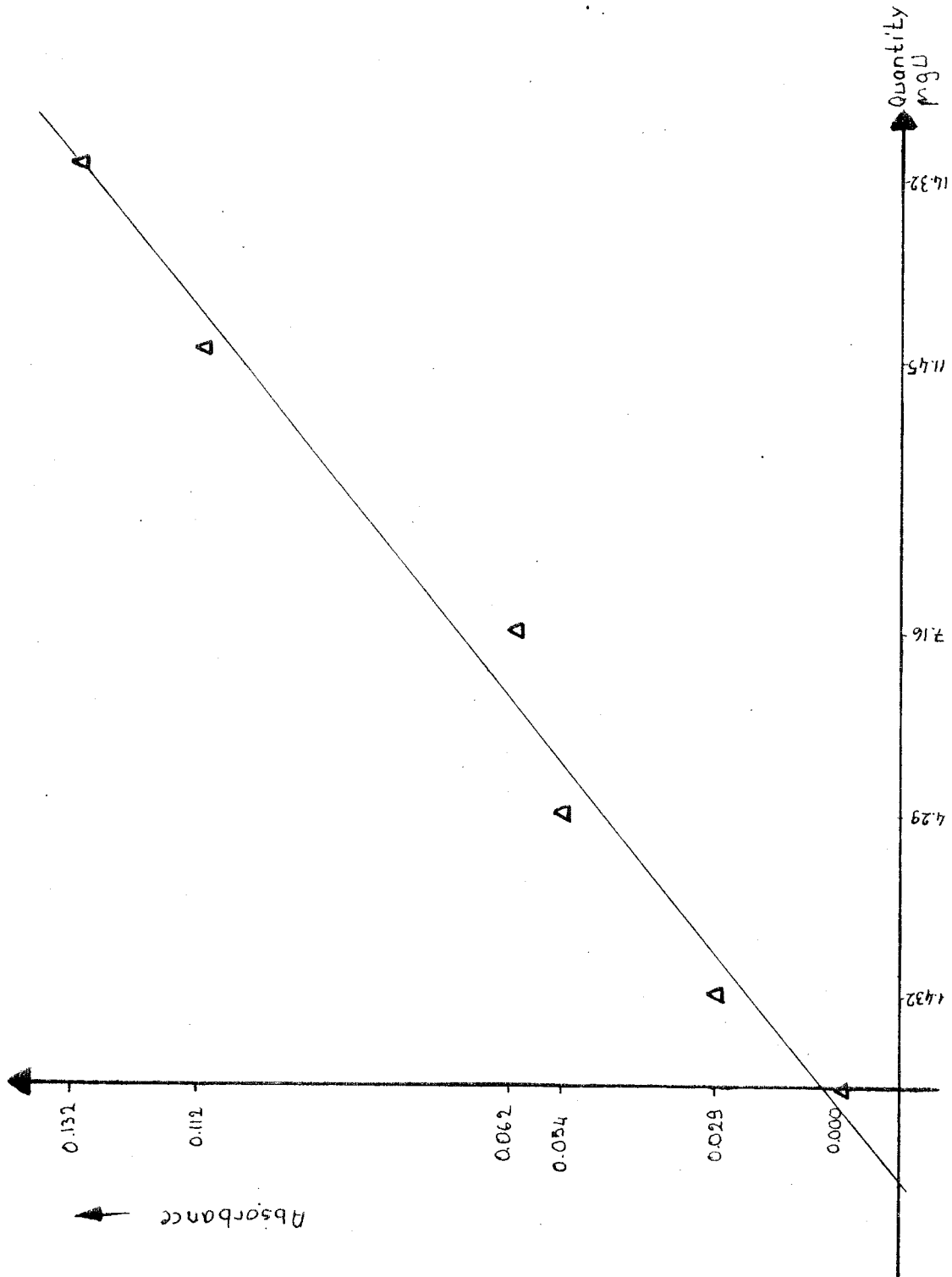
Fig. 6.3- Analysis of the sediment with multiple standard addition method. (PA 74, JO 71)
(Standard deviation of this fit is found to be 0.00682).
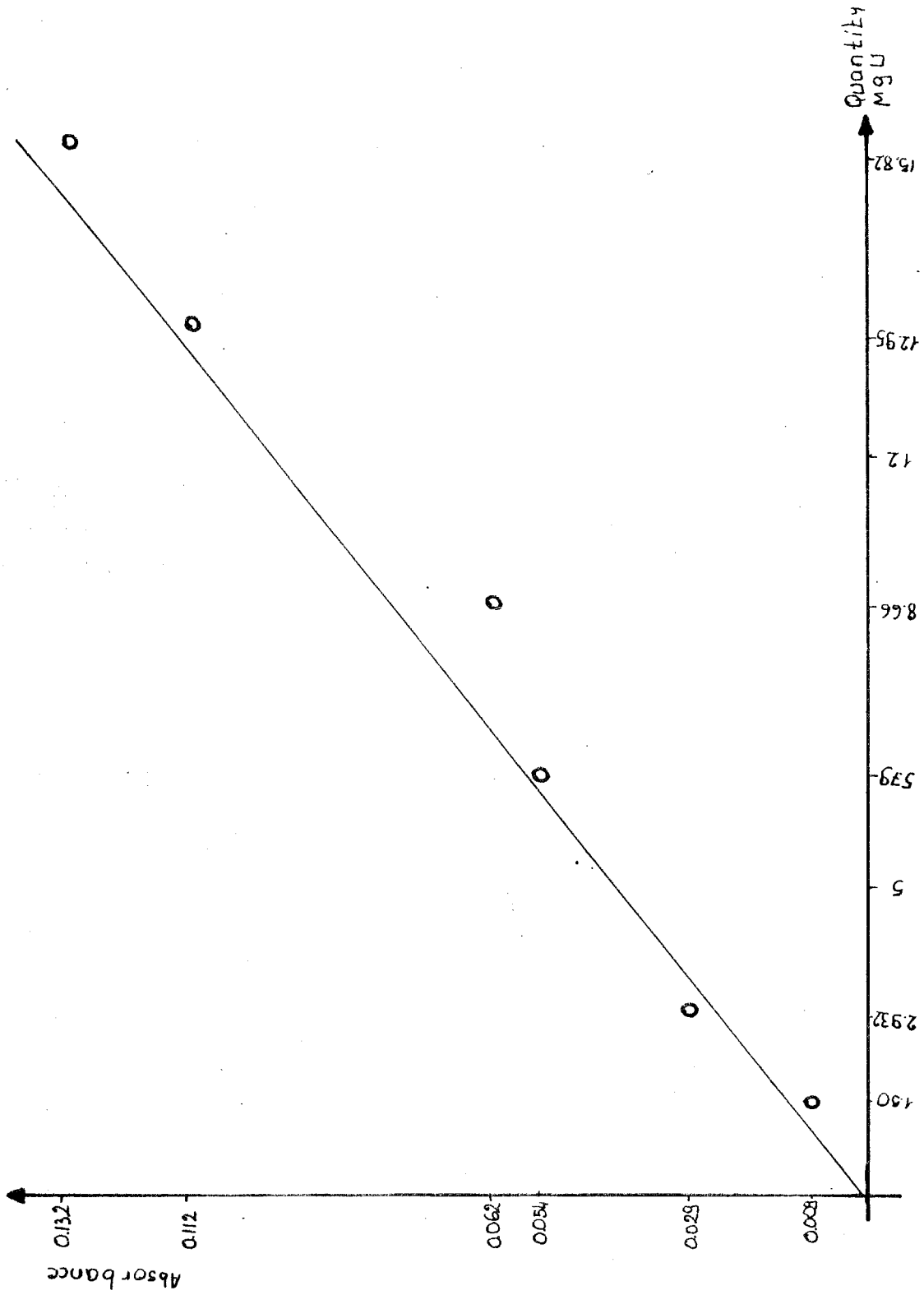
Fig.6.4- Calibration curve prepared by passing the standards from decomposition step (PA 74) (Standard deviation of this fit is found to be 0.00682).

TABLE 6.12- RESULTS FOR CALIBRATION CURVE

Sample	I	II	III	IV	V	VI
Concentration µgU	1.5	2.932	5.79	8.66	12.95	15.82
Absorbance	0.009	0.029	0.054	0.062	0.112	0.132

Least squares method was applied also to Fig.6.3 and 6.4 and are shown in Appendix I.

In the view of the results the analytical procedure was determined as follows.

0.2 gr. of sample of variable mesh size is put in teflon crucible. 1 ml of aqua regia (3 ml HCl + 1 ml HNO_3) is added, after the sample is completely wetted 3.6 ml of HF of 40% is added and the crucible is closed, placed in the steel bomb closed tightly and the vessel is placed in an air oven for two hours at 190°C than cooled to ambient temperature with the aid of a hair drier blowing unheated air in about 25 minutes. 1.3 gr of boric acid is dissolved in 20 ml of water and the decomposed sample is transferred in to boric acid solution (PA 74) and diluted to 30 ml with water.

5.0 ml of 2% (w/v) sodium fluoride and 2.0 ml of freshly prepared 5% ascorbic acid solution is added and mixed. 3.0 ml of 0.1 M TOPO solution is added to the mixture and extracted for 1 minute. 2.0 ml of organic phase is pipetted in to a 25 ml volumetric flask. 1.0 ml of dilute complexing solution, 4.0 ml of 0.05% bromopadap and 2.0 ml of pH 8.35 buffer is added and allowed to stand for 10 m and diluted to volume with ethanol and, then the colour is measured against a reagent blank, carried out through the procedure at 578 nm (JO 71).

6.F. FLOTATION EXPERIMENTS

A flotation operation follows a series of steps. Primarily the grain sizes of the minerals must be suitable to float otherwise they cannot be concentrated by floating. In the second step liberation of the particles must be achieved. Liberation means that each particle of ore, formed of valuable mineral or worthless gangue, is separated only as nearly as possible. If the above conditions are not achieved grinding and crushing of the ore is necessary. Then the ore is reacted with certain reagents to increase the effectiveness of the flotation operation. These reagents serve as activating, modifying, depressing and frothing agents. These reagents could be added at the grinding circuit, conditioning circuit and/or flotation circuit, according to the results of the tests performed prior to a complete operation. During the flotation operation the froth collected at the top contaning the concentrated ore is removed for further treatment.

The reagents that were used in this study and their characteristic properties are given in Table 6.13.

The type of flotation cell used in these experiments is of the agitation type, aired mechanically by the movement of the stirrer. The schematics of the flotation equipment used in this study is shown in Fig.6.5. A description of a flotation experiment is as follows. The flotation cell is 281 ml. Pulp density is taken as 20 %, this means 50 gr of sediment (dry) plus 200 gr of water and a glass rod is used as a stirrer. The cell is primarily used as a conditioner while continuously stirring, 0.5 cc of 0.97-0.95 m sulfuric acid is added to adjust to the required pH. Sulfuric acid also helps to depress quartz. Then 0.005 gr Na_2SiO_3 is added which is a selectivity agent for uranium (Table 6.13) and conditioned for 5 m. Then 0.005 gr of $FeCl_3$ is added which is an activating agent for

uranium minerals (Table 6.13) and mixed for 5 m. After that
0.0027 gr of aeroxanthate 301 is added (Table 6.13) and mixed
for 5 minutes followed by a frothing agent, aerofroth 65
(Table 6.13), is added and mixed for 2 m. Then the glass rod
is changed with glass pipe and flotation is performed for the
required time duration and froth accumulated at the mouth of
the cell is removed. The pH meter used for the pH measurements is of
photovolt company N.Y.city Cat No 1199. The reagents that
were used in these experiments mainly are the products of the
American Cyanamid Company with the properties given in Table
6.13.

A measure to calculate the efficiency in flotation
opeations is recovery. Recovery, R, is the proportion of the
valuable part in the concentrate to the valuable part in the
feed and is calculated as follows (AT 74):

$$R = 100 \cdot \frac{C \cdot c}{F \cdot f}$$

F: Feed rate of the ore in tons,
f: Mineral content of the ore,
C: Amount of the concentrate, in tons,
c: Mineral content of the concentrate.
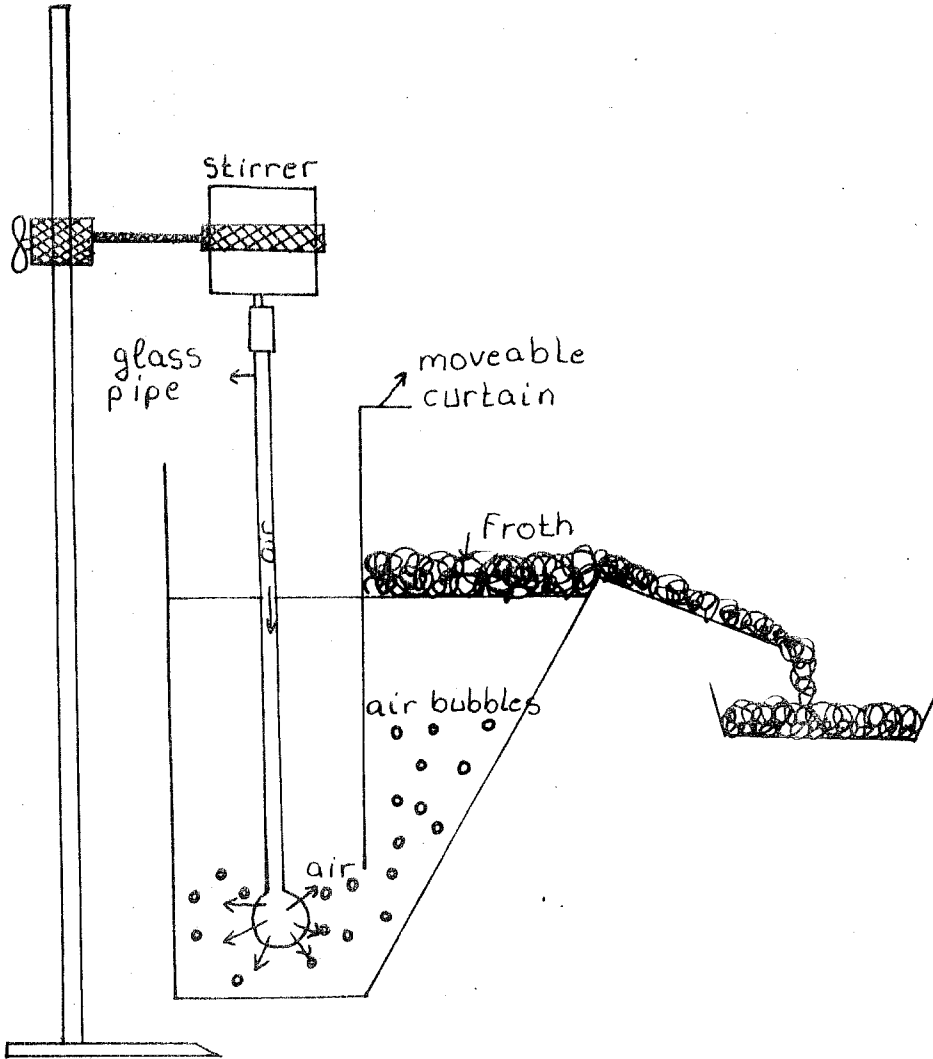
Fig.6.5- The schematic of flotation equipment used in this study.
(Supplied by Mr.Akın Yılmaz of GÖL A.Ş.)

TABLE 6.13– LIST OF REAGENTS USED IN THE FLOTATION EXPERIMENTS

Reagent	Formulation	Grade	Properties	Addition Point	Usual Dosage g/ton	Source	Reference
Sodium Silicate	Na_2SiO_3	60%	Disperse gangue slimes Depress quartz and silicates Assists selectivity of uranium minerals.	Any point	250-1500	Industrial origin	ACC
Ferric Chloride	$FeCl_3$		Activates uranium minerals	Conditioner circuit	50- 500		ACC
Lead nitrate	$Pb(NO_3)_2$		Activator for uranium minerals	Conditioner circuit	50-1000		ACC
Lead acetate	$(CH_3COO)_2Pb$		Activator for uranium minerals	Conditioner circuit	50-1000		ACC
Aerofloat 208	Sodium diethyl and sodium disecondary butyldithio phosphate		Suitable for metals such as gold, copper and silver and decided to give good results for uranium minerals also	Any point	5- 50	ACC	ACC
Aerofloat 242			Used for recovery of uranium compounds in mine water by ion flotation	Conditioning and flotation circuits	10- 75	ACC	–
Aero xanthate 301	Sodium Secondary butyl xanthate		Useful in flotation of Pb, Co, Ni and precious metals, gives good results for uranium minerals also	Conditioning and flotation circuits	25- 75	ACC	ACC

TABLE 6.13- LIST OF REAGENTS USED IN THE FLOTATION EXPERIMENTS (Continued)

Reagent	Composition		Description	Point added	Dosage		
Aero Promoter 404			Good for lead and precious metals and was also suitable for uranium minerals	Any point	25- 250	ACC	ACC
Aero Promoter 710	Sodium soap of a crude fatty acid		Used in removal of heavy mineral impurities from glass sand, flotation of precious metals and principal promoter for uranium carnotite	Conditioner and flotation circuit	100-1000	ACC	ACC (AT 74)
Aero promoter 830 and 845	Anionic sulphonates		Used in removal of heavy minerals from glass sand and was considered to give good results for uranium also	Flotation circuit	150- 250	ACC	ACC
Aeromine 3037	Amine Salts		Principal promoter for uranium pitchblende and used as a reagent in ion flotation	Conditioner of flotation circuit	50- 250	ACC	ACC and (-)
Aerofroth 65	Water soluble polyglycol		Used for lead and precious metals and frothing agent for Pitchblende	Conditioner or flotation circuit	5- 100	ACC	ACC
Aerosol GPG	Anionic Di (2-ethyl hexyl)sodium sulfosuccinate		Used as a leaching aid for uranium ores since it is a surface active agent it was decided it will improve the flotation of uranium	Conditioning point	25- 150	ACC	ACC
Sulfuric acid	H_2SO_4	0.95- 0.97m	Used for pH adjustment Assist recovery of gold	Conditioning circuit	250-2500	ACC	ACC
Sodium hydroxide	NaOH		Used for pH adjustment	Conditioning circuit	250-2000	ACC	ACC

ACC: American Cyanamid Company. The flotation reagent and the flotation cell were obtained from Mr.Akın Yılmaz of GÖL A.Ş.

CHAPTER 7

EXPERIMENTAL RESULTS AND THE DISCUSSION OF RESULTS

This chapter will cover the discussion of the results obtained from the experiments. In the first part the results of the spectrophotometric method and the steps taken during the study is discussed. In the second part the analysis of the results of the flotation experiments and their discussion is given.

7.A. DETERMINATION OF WATER CONTENT OF THE SEDIMENT

Four samples were taken from the core before mixing it completely to obtain a homogenous mixture. The results varied between 12-25%. There is almost 35% deviation from the mean. These values are lower than those reported by a previous work which had indicated as 50-55% non bonding water(3). The drying at $105^{\circ}C$ of sediments rich in coccolith and organic carbon give 85% weight loss according to a previous work(3).

7.B. COMBUSTION EXPERIMENTS OF THE SEDIMENTS

Some previous studies on Black Sea sediments indicated that the sediments are rich in organic matter (DE 77)(3), that the burning of sediments will lead to a considerable weight loss and may facilitate the production of the ore. But an important point

is that above 400°C uranium passes from hexavalent state to tetravalent state which creates difficulties at leaching and separation steps. The results obtained are shown in Table 6.1. The samples taken for combustion primarily were dried at 105°C. The results were not as expected. Although there is an increase in weight loss with temperature this could be due to bonded water loss. Because of some difficulties encountered during experiments it was not possible to use the same time period for every experiment and this differance could be the cause of this discrepancy. According to some previous work(3) the organic carbon content varies between 0.35%-14.25% and weight loss of sediment due to combustion was reported as between 30%-35%(3).

7.C. DETECTION AND DETERMINATION OF URANIUM IN STANDARD SOLUTIONS

A preliminary experiment was carried out to become acquainted with the method and the reagent. The study was performed as described in 6.E.i. The results are shown in Table 6.2. Sample 4 is the blank whose absorbance was measured versus ethanol and the other three were measured versus blank. The values are marked on Fig.7.1. Since Beer's law is obeyed between 0-1.3 absorbance units (0-4.2 µgU/ml in the final solution) (JO 71). Sample 1 showed great diversity. The straight line on the Fig.7.1 indicates that Beer's law is obeyed up to 4 µgU/ml concentration as stated in (JO 71).

7.D. PRIMARY ANALYSIS FOR DETERMINATION OF URANIUM IN SEDIMENTS USING 5.0 ml TOPO SOLUTION

Analysis of the sediments were carried out by addition of standards. The results obtained are shown in Table 6.4. Sample A in Table 6.4 is not in agreement with sample 1 in Table 6.3 which is taken as an aliquot of 80 µgU initially

and yields a final solution of 1.28 µgU/ml. Sample A might
have given a higher value than sample 1 since it is 80 µgU
plus the amount of uranium in the sediment. But comparing
sample B in Table 6.4 with sample 7 in Table 6.3, which is a
final solution of 1 µgU taken initially, an agreement is
observed, because the absorbance of sample 7 is 0.008 and the
absorbance of sample B, which is 1 µgU plus the amount of
uranium in sediment, is 0.015. It is clear that sample B
contains uranium more than 1 µgU, thus it gives a higher
absorbance reading. But the difference between samples A and
1 is 0.011 absorbance units. Since it was predicted (JO 71)
that excess NaF depresses uranium the following experiments
were performed by eliminating the sodium fluoride added. The
results are shown in Table 6.5. To become sure of the absor-
bance values obtained directly from the sediments, the stan-
dard added sediments were measured against the standard of 5
µgU (or 0.08 µgU/ml in the final solution). The values are
close to each other. The instrument is not sensitive for low
values for example to measure a difference of 0.002 absorbance
units.

Another group of experiments were carried out by adding
sodium fluoride (2% w/v) as described in (PA 74). The results
are listed on Table 6.6.

Comparison of Table 6.5 with table 6.6 shows that
sodium fluoride effects the measurements considerably, and
below 7.16 µgU level (0.115 µgU/ml in the final solution) the
method could not retain its sensitivity for determination of
uranium or a more sensitive instrument may be needed.

Another source that could be a problem was silicon
dioxide because the silicon dioxide which was used to prepare
silicafluoroboric acid (PA 74) was not of analytical grade.
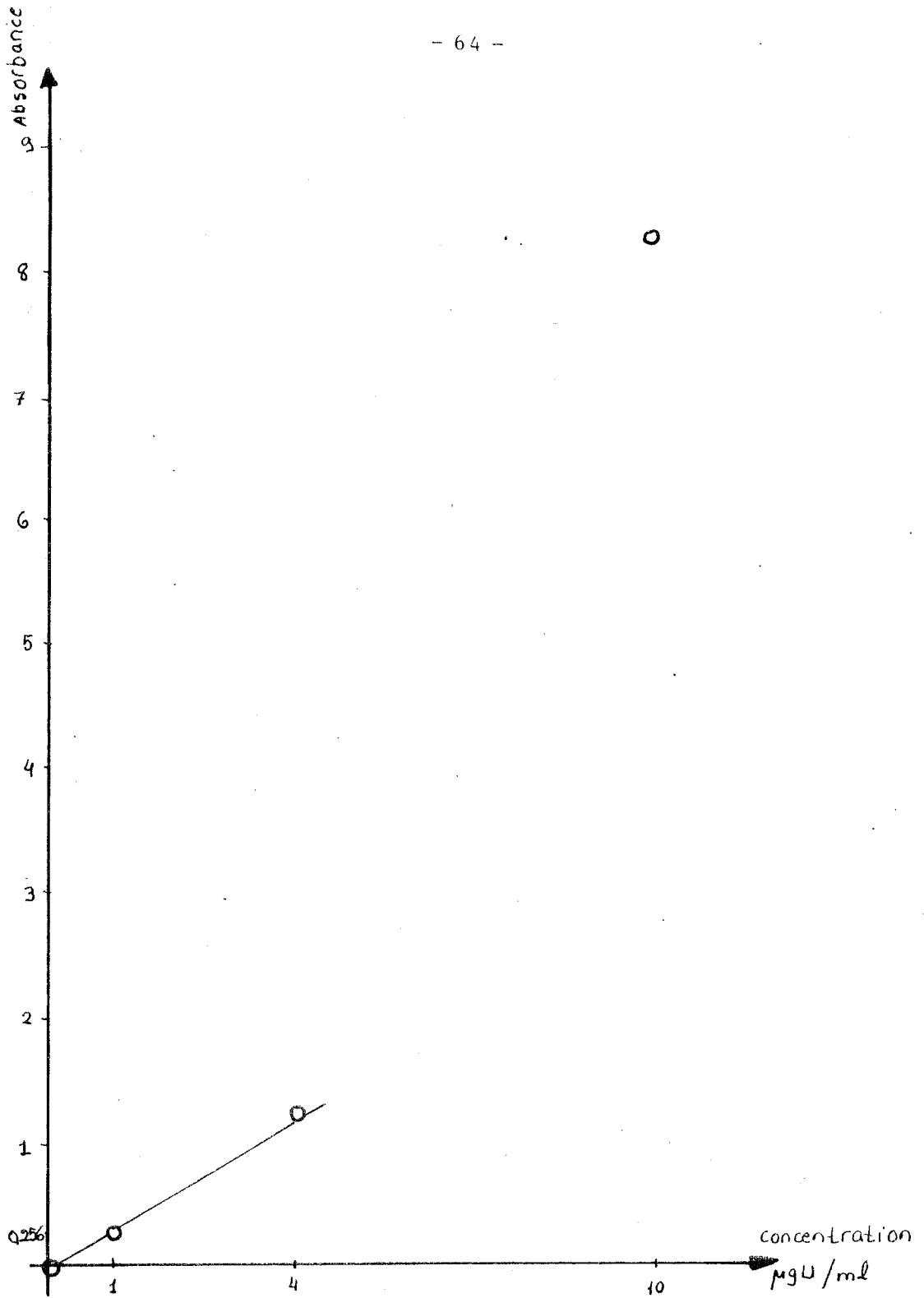
Fig.7.1– Concentration of uranium in standard solutions versus absorbance.

Silicon dioxide was passed through the decomposition procedure and was measured against a blank prepared with distilled water only. The results are shown in Table 6.7. Both measurements in Table 6.7 were taken versus ethanol. As it can be seen from the table, there is no considerable difference, so silicon dioxide can be considered as uranium free.

7.E. THE SECOND STEP IN ANALYSIS FOR DETERMINATION OF URANIUM IN SEDIMENTS USING 3.0 ml TOPO SOLUTION

The amount of TOPO was decreased to 3.0 ml and the amount of the ore was increased to 2.0 gr as an alternative to increase the sensitivity of the measurements. The experiments based on 2.0 gr of sediment gave the results reproduced in Table 6.9. The results indicate that the uranium content is between 1-2 ppm. A further step was performed to compare the decomposition in the open teflon cup with the decomposition procedure described in (PA 74). As can be seen from Table 6.10. the decomposition of 71.6 μgU gives a higher absorbance value with the procedure of (PA 74) than the one used with open teflon cup.

7.F. FINAL FORM OF ANALYSIS FOR DETERMINATION OF URANIUM IN SEDIMENTS

In view of the above results a new calibration curve was prepared and standard addition method was applied for the determination of uranium content of the sediments. The results are shown in table 6.11, 6.12 and marked on Fig.6.3 and 6.4. From those graphs the amount of uranium was determined as 7.5 ppm.

7.G. RESULTS OF THE FLOTATION EXPERIMENTS AND DISCUSSION

7.G.i. The First Group of Flotation Experiments

The first flotation experiments were deviced to observe

the effects of some parameters (time, quantity etc) and the effects of different reagents on the recovery of uranium as listed on Table 7.1.

Recovery is calculated as shown in Chapter 6 using the formula

$$R = 100 \cdot \frac{\text{Amount of concentrate x Mineral content of concentrate}}{\text{Amount of feed x Mineral content of feed}}$$

As a numerical example the following is given. For experiment 1 in table 7.1, amount of concentrate is 3.11 g, its mineral content is 11.75 ppm, amount of feed is 50 g and its grade is 5 ppm, inserting these values, the recovery becomes

$$R = 100 \times \frac{3.11(g) \times 11.75(ppm)}{50(g) \times 75 \ (ppm)} = 9.74\%$$

In experiment 1 Aeromine 3037 was used as a promoter(1), $FeCl_3$ as an activator for uranium minerals, Na_2SiO_3 depressant for silica containing minerals, because the sediment contains clay minerals (DE 77) and aerofroth 65 as a frothing agent. Aeromine 3037 is a cationic type promoter so it is an electron acceptor, and for this reason it is suitable for use in the basic range of the pH scale, otherwise in high acidic range it could decompose and become useless. It was also used in combination with other promoters. In experiment 4 it was used together with promoter and was found suitable for most flotation operations of uranium minerals (AT 74)(3). But the combination of both gave a very low recovery. The reason could be a reaction between the two promoters, because promoter 710 is a fatty acid which is an electron donor and aeromine 3037 is an amine which is electron acceptor. Another point was the change of the pulp density. It was an observed fact that while pulp density decreases the mineral content of the concentrate increases and the recovery passes through an optimum

TABLE 7.1- THE FIRST GROUP OF FLOTATION EXPERIMENTS

Experiment No	Reagents	Quantity (gr)	Conditioning time (minutes)	Pulp density %	pH	Flotation time (minutes)	Amount of Concentrate (gr)	Mineral Content of Concentrate (ppm)	Recovery %
1	Na2SiO3 FeCl3 Aeromine 3037 Aerofroth 65	0.005 0.005 0.0023 0.0019	15 15 15 10	20	8.1	5	3.11	11.75	9.74
2	Na2SiO3 FeCl3 Aeropromoter 710	0.01 0.01 0.0333	15 15 15	20	8	3	4.17	10	11.12
3	Na2SiO3 FeCl3 Aeropromoter 845	0.005 0.005 0.011	15 15 17	20	8.08	3	2.14	5.5	3.14
4	Surface active GPG Pb(NO3)2 Aeropromoter 710+ Aeromine 3037	0.011 0.0266 0.0333+ 0.0023	10 10 20	11	10	3	2.66	1.25	1.77
5	(CH3COO)2 Pb Aeropromoter 404 Aerofroth 65	0.020 0.0057 0.0019	15 15 1	11	10	5	3.03	7	11.31
6	Na2SiO3 Pb(NO3)2 Aeroxanthate 301+ Aerofloat 242+ Aeropromoter 404 Aerofroth 65	0.005 0.0266 0.0027+ 0.0078+ 0.0057 0.0019	10 15 25 1	11	10.2	8	3.10	9	14.88

TABLE 7.1- Continued

No.	Reagent								
7	Na2SiO3	0.005	15	11	10	4	4.15	8.5	18.81
	Surface active GPG	0.011	22						
	+ (CH3COO)2Pb	+0.024							
	Aerofloat 242+	0.0078+	20						
	Aeromine 3037	0.0023	1						
	Aerofroth 65	0.0019							
8	Na2SiO3	0.005	15	11	3.3	3	3.79	4.25	8.59
	Surface active GPG	0.011	10						
	FeCl3	0.005	15						
	Aero xanthate 301+	0.0027+	15						
	Aerofloat 208	0.0035	1						
	Aerofroth 65	0.0038							
9	Na2SiO3	0.005	10	11	4	3	2.37	11.5	14.53
	Surface active GPG	0.011	10						
	Pb(NO3)2	0.0266	10						
	Aeropromoter 404+	0.0057+	20						
	Aerofloat 242	0.0078	1						
	Aerofroth 65	0.0039							
10	Na2SiO3	0.005	10	11	5.1	5	4.33	6	13.85
	Pb(NO3)2	0.0266	10						
	Aeropromoter 710+	0.0333+	30						
	Aeropromoter 830	0.0089							

value. This was observed for copper in (TA 45). For this reason in flotation operations the pulp density is usually taken between 25-30% (TA 45).

In experiment 7 Aeronime 3037 gave the highest recovery among other experiments with combination of aeropromoter 242. The pH value of pulp was 8.1 which was its natural pH. while the pH level of experiment 7 was obtained by addition of sodium hydroxide. In the flotation experiments as a whole the most desirable values were obtained when pH was about 10 as can be seen from Table 7.1.

The most desirable values for recovery were obtained when pulp density was 11% while the recovery remained lower when pulp density was 20%. This was expected as stated in (TA 45). But the drawback of low pulp density is that it decreases the flotation efficiency considerably.

The time required for flotation or froth collection seems to give the best results between 3 and 8 minutes. High froth collection time could increase flotation cost and another fact is that the gangue minerals start appearing in the froth.

The conditioning time periods used, range between 10 and 20 minutes. These values are usually chosen for most flotation operations, but the range may vary from 5 minutes to 3 hours (TA 45) in practice.

Among promoters aerofloat 242 which is of the aryl dithiophosphoric acid type gave the most desirable results with combination of other promoters; the highest recovery was reached with aerofloat 242 and aeromine 3037 mixture.

With experiments 8,9 and 10 the effect of low pH (acidic range) on flotation was observed. Although there was an increase in recovery, the ore changes its structure because above pH 6 the sediment begins to decompose. For this reason the most suitable pH range for this work appears to be in the basic range.

7.C.ii. The Second Group of Flotation Experiments.

The second group of the experiments were performed to observe the effects of some parameters such as froth collection time, pH change and conditioning time variation. The results are summarized on Table 7.2.

From experiments 1,2,3 and 4 on Table 7.2, the variation of the amount of concentrate with flotation time can be observed. Fig.7.2 shows that as the time for froth collection increases the quantity of froth obtained also increases. In these experiments the amount of concentrate increases up to about 5 minutes of flotation time and doesn't show a considerable change from 5 minutes up to 10 minutes. The relation between recovery and froth collecting time is shown on Fig.7.3. The figure indicates that increasing the flotation time does not give high concentrations and an extremum value is obtained for 5 minutes of froth collecting period.

The experiments 2 and 5 were done to observe the effect of conditioning time variation on recovery and concentrate for froth collection time of 3 minutes. The results are shown graphically on Fig.7.4 and 7.5 respectively. While recovery remains nearly the same the weight of concentrate increases faster. This is undesirable simply because this decreases the efficiency of the operation, in other words this means there is no separation, so there is no flotation. The experiments 3 and 6 were performed for froth collection time

TABLE 7.2- RESULTS OF FLOTATION EXPERIMENTS OBTAINED BY CHANGING PARAMETERS SUCH AS FLOTATION TIME, pH AND CONDITIONS TIME

Experiment No	Reagents	Quantity (gr)	Conditioning time (minutes)	Pulp density %	pH	Flotation time (minutes)	Amount of Concentrate (gr)	Grade of Concentrate (ppm)	Recovery %
1	Na_2SiO_3 $FeCl_3$ 208+ 301+ 710+ 845	0.01148 0.01 0.0035+ 0.0027+ 0.0333+ 0.011	17 15 60	20	8.1	1	0.80	7	1.49
2	Na_2SiO_3 $FeCl_3$ 208+ 301+ 710+ 845	0.01148 0.01 0.0035+ 0.0027+ 0.0333+ 0.011	17 15 60	20	8.1	3	5.85	11	17.16
3	Na_2SiO_3 $FeCl_3$ 208+ 301+ 710+ 845	0.01148 0.01 0.0035+ 0.0027+ 0.0333+ 0.011	17 15 60	20	8	5	9.55	12.5	31.83
4	Na_2SiO_3 $FeCl_3$ 208+ 301+ 710+ 845	0.01148 0.01 0.0035+ 0.0027+ 0.0333+ 0.011	17 15 60	20	8.2	10	10	10	26.67

TABLE 7.2- Continued

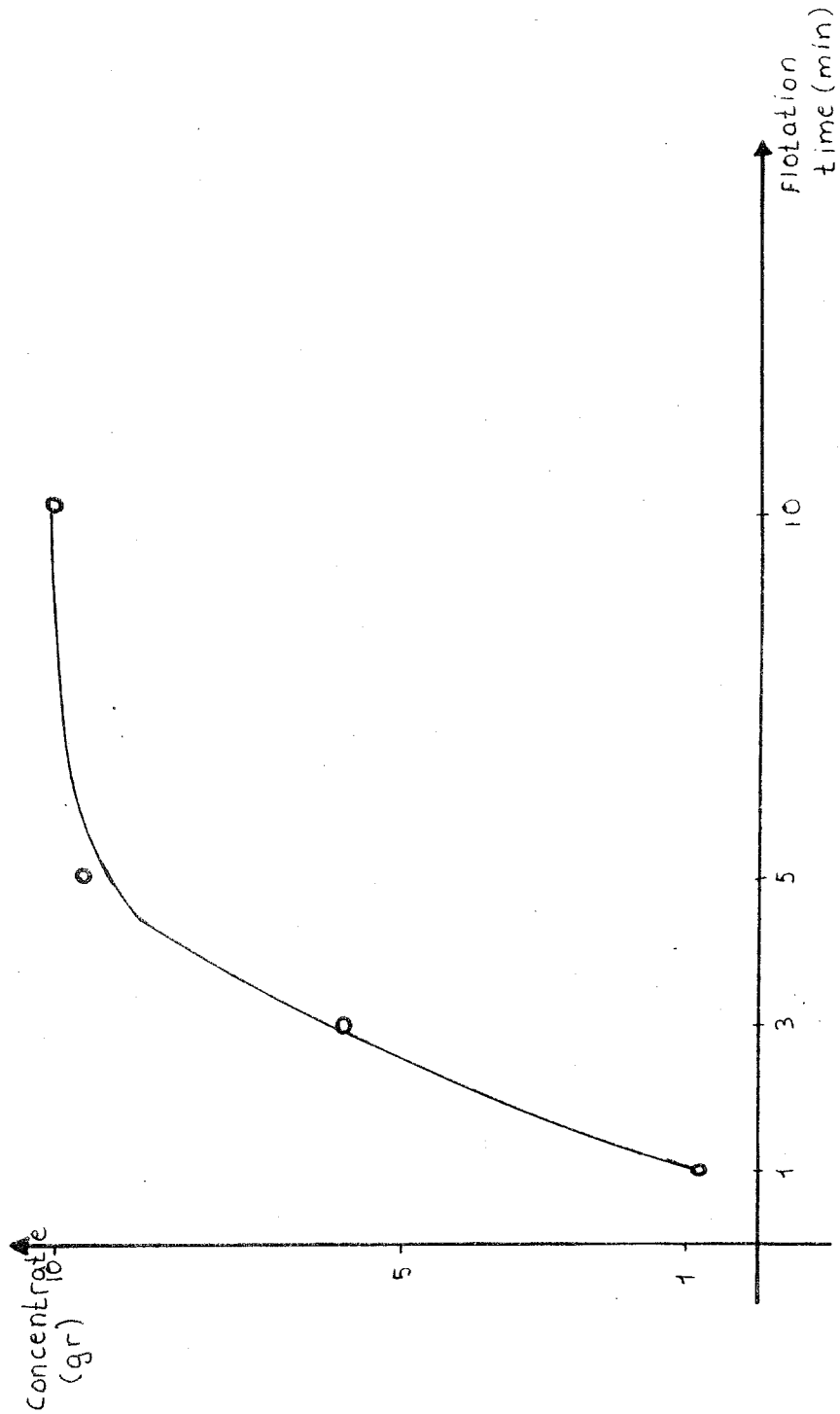|									
5	Na2SiO3	0.01148	17	20	8.1	3	7.74	9.5	19.61
	FeCl3	0.01	15						
	208+	0.0035+							
	301+	0.0027+							
	710+	0.0333+							
	845	0.011	180						
6	Na2SiO3	0.01148	17	20	8.2	5	8.7	7.75	17.98
	FeCl3	0.01	15						
	208+	0.0035+							
	301+	0.0027+							
	710+	0.0333+							
	845	0.011	180						
7	Na2SiO3	0.005	5	20	6	10	5.35	3.07	4.38
	FeCl3	0.005	5						
	301	0.0027	5						
	65	0.0019	2						
8	Na2SiO3	0.005	5	20	8	10	2.53	3.2	2.16
	FeCl3	0.005	5						
	301	0.0027	5						
	65	0.0019	2						
9	Na2SiO3	0.005	5	20	10	10	3.86	4.27	4.39
	FeCl3	0.005	5						
	301	0.0027	5						
	65	0.0019	2						
10	Na2SiO3	0.005	5	20	12	10	4.9	3.5	4.57
	FeCl3	0.005	5						
	301	0.0027	5						
	65	0.0019	2						

Fig.7.2.- The amount of concentrate obtained as a function of the flotation time.
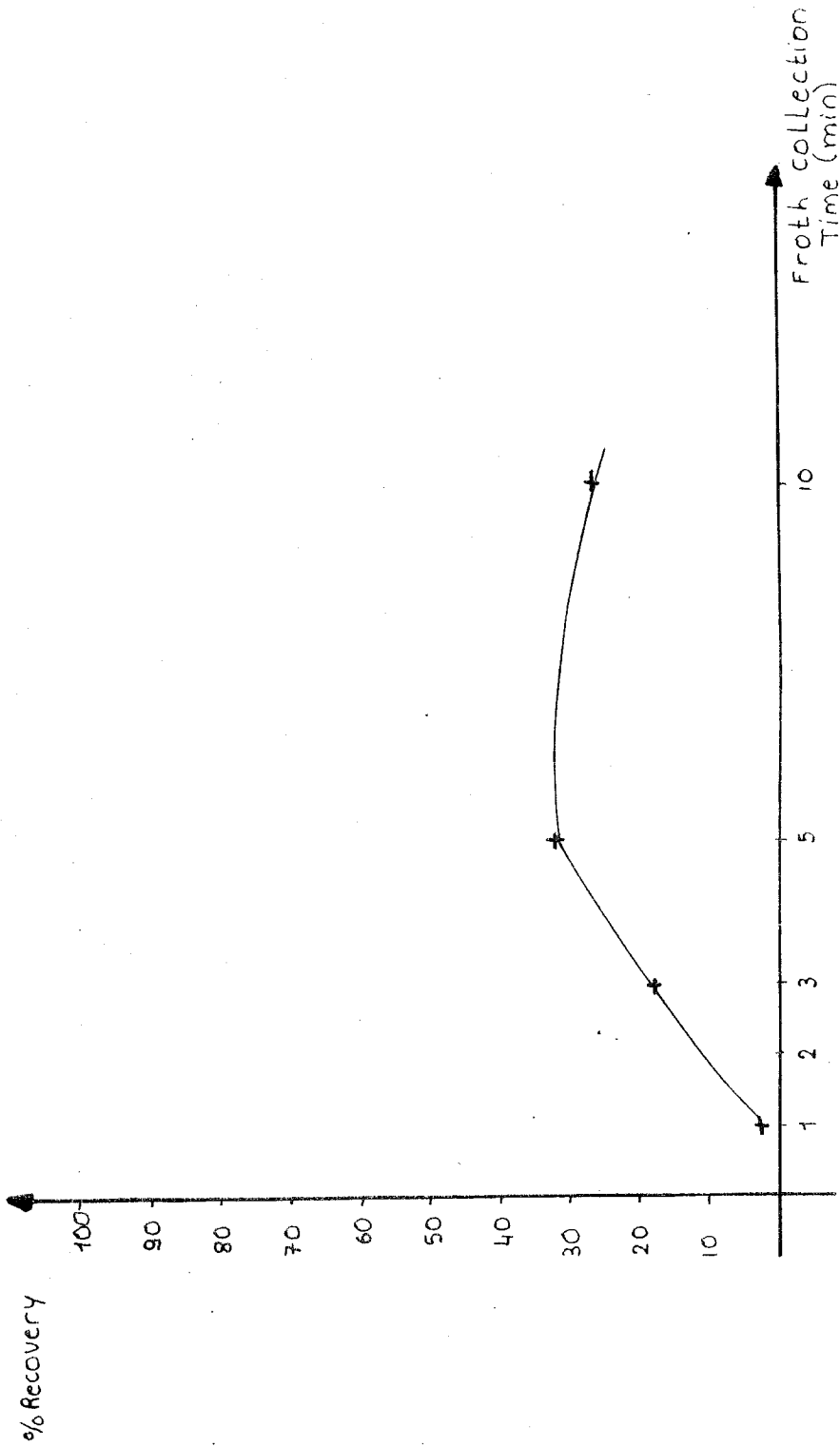
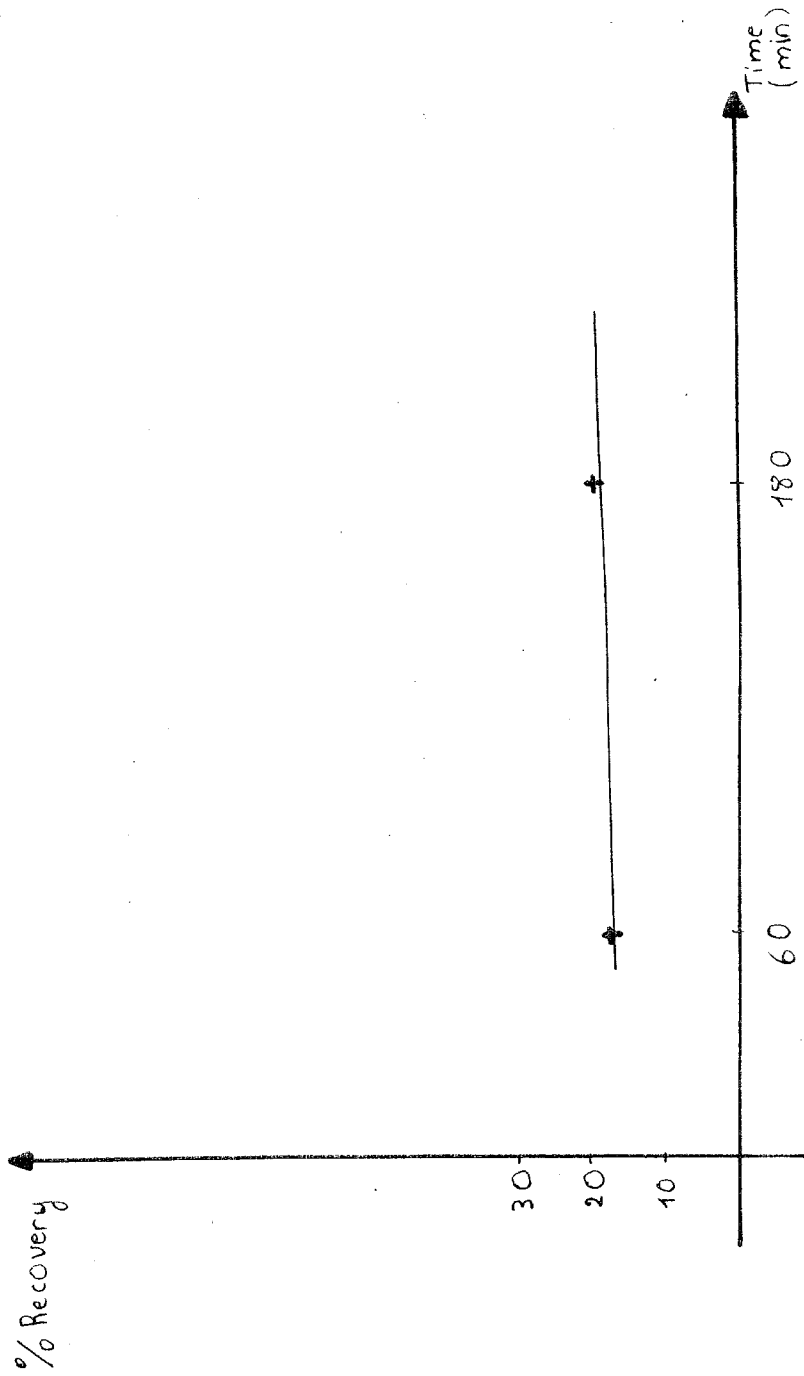Fig. 7.3- The change of Recovery as a function of flotation time.

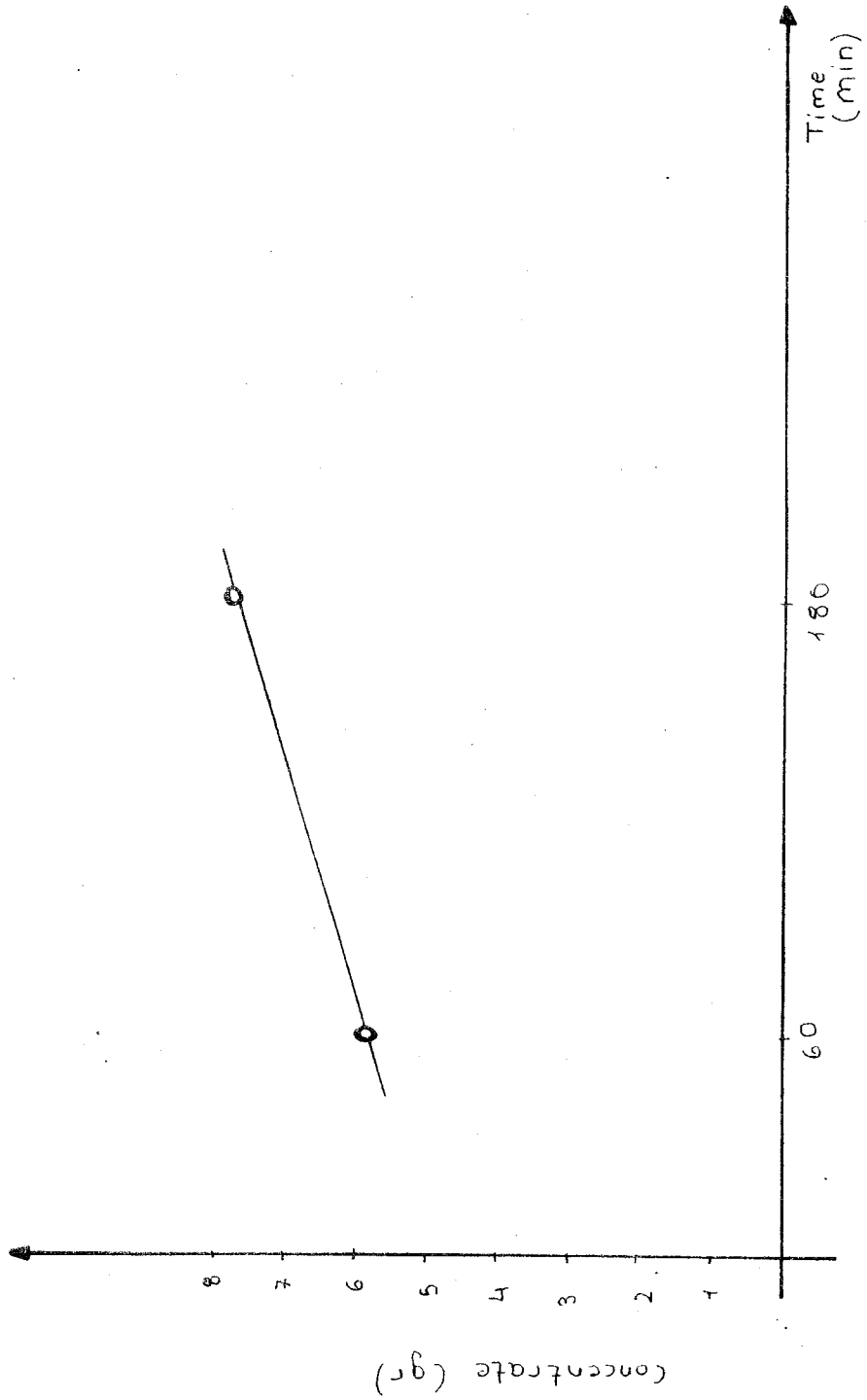Fig.7.4- The change on Recovery of a function of conditioning time (Flotation time 3 minutes).

Fig.7.5- The change of concentrate amount as a function of conditioning time. (Flotation time 3 minutes).

of 5 minutes. The results are given graphically on Fig.7.6 and 7.7. A comparison of Figures 7.4, 7.5, 7.6 and 7.7 shows that longer conditioning time is not necessary because it does not have any effect on flotation efficiency.

The experiments through 1 to 6 in Table 7.2 were performed without the addition of a regulating agent. Because the pulp obtained has a pH of about 8, these experiments were carried out for pH of 8. The effect of pH variation was observed on the succeeding experiments 7,8,9 and 10 respectively. The analysis of these experiments were done by using only the teflon crucible for decomposition of the tailing and concentrate, which gave relatively low values for uranium content in sediments, hence the recovery obtained for these experiments might seem lower than the previous ones.

The results are shown an Fig.7.8 and 7.9. The graphs showed that flotation of sediments at their natural pH (when pH was 8) was not found advantageous according to the parameters used in these experiment. The best conditions were obtained when pH was equal to 10.

7.H. SUMMARY

The combustion of the sediment didn't give the results expected (i.e. high weight loss at high temperatures was not obtained) as suggested in some previous studies (DE 77)(3). Analytical step was performed similarly to the description in (JO 71) and (PA 74) but by restricting the amount of TOPO solution to 3.0 ml.

In flotation experiments the best results were obtained with Aerofloat 242, aeromine 3037 also aeropromoter 710 and 404 gave high recoveries. Acidic range of the pH scale was not found attractive. In a total of 20 flotation experiments the best recovery was obtained from experiment 3 Table 7.2.
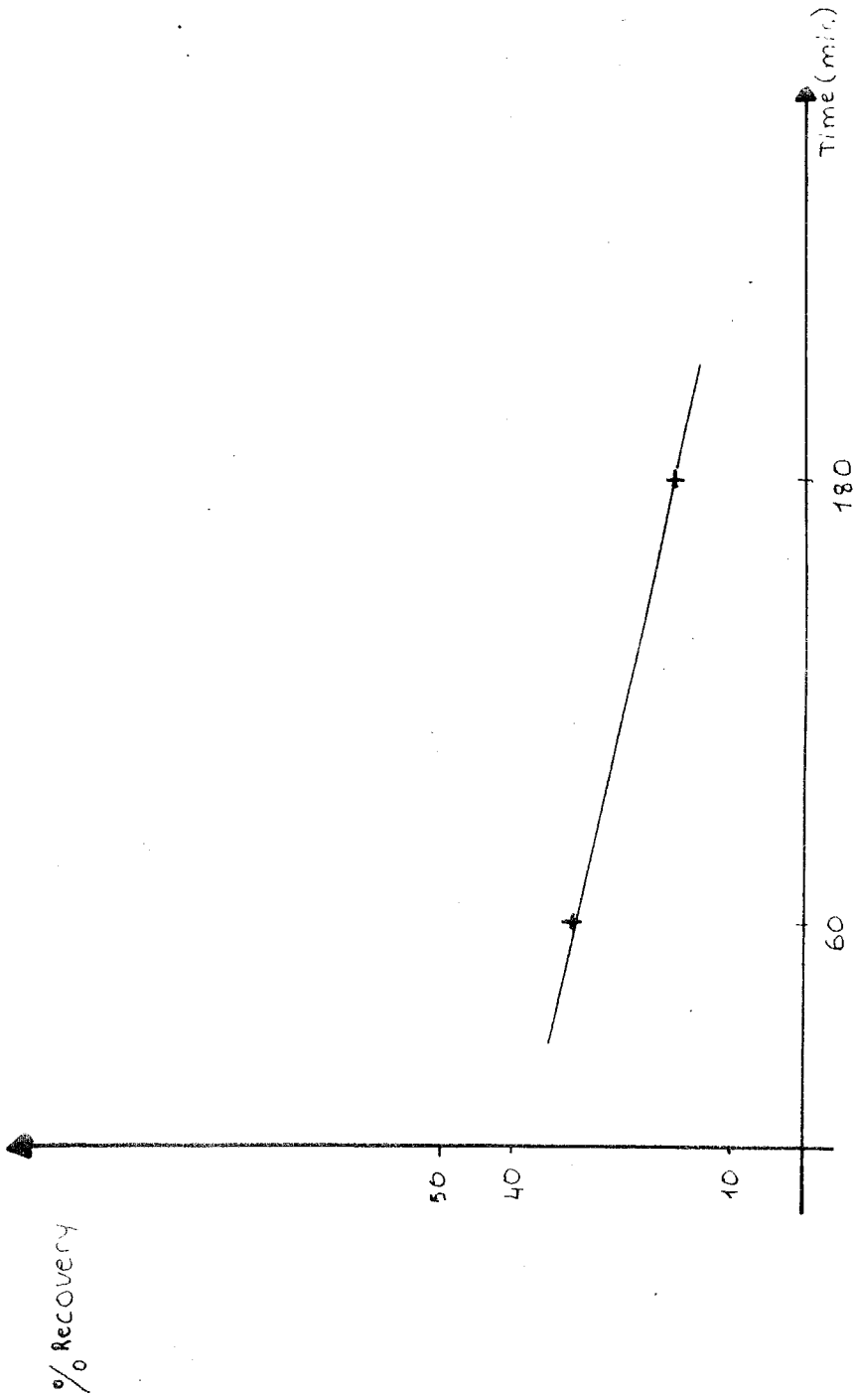
Fig.7.6- The change of Recovery as a function of conditioning time (Flotation time 5 minutes).
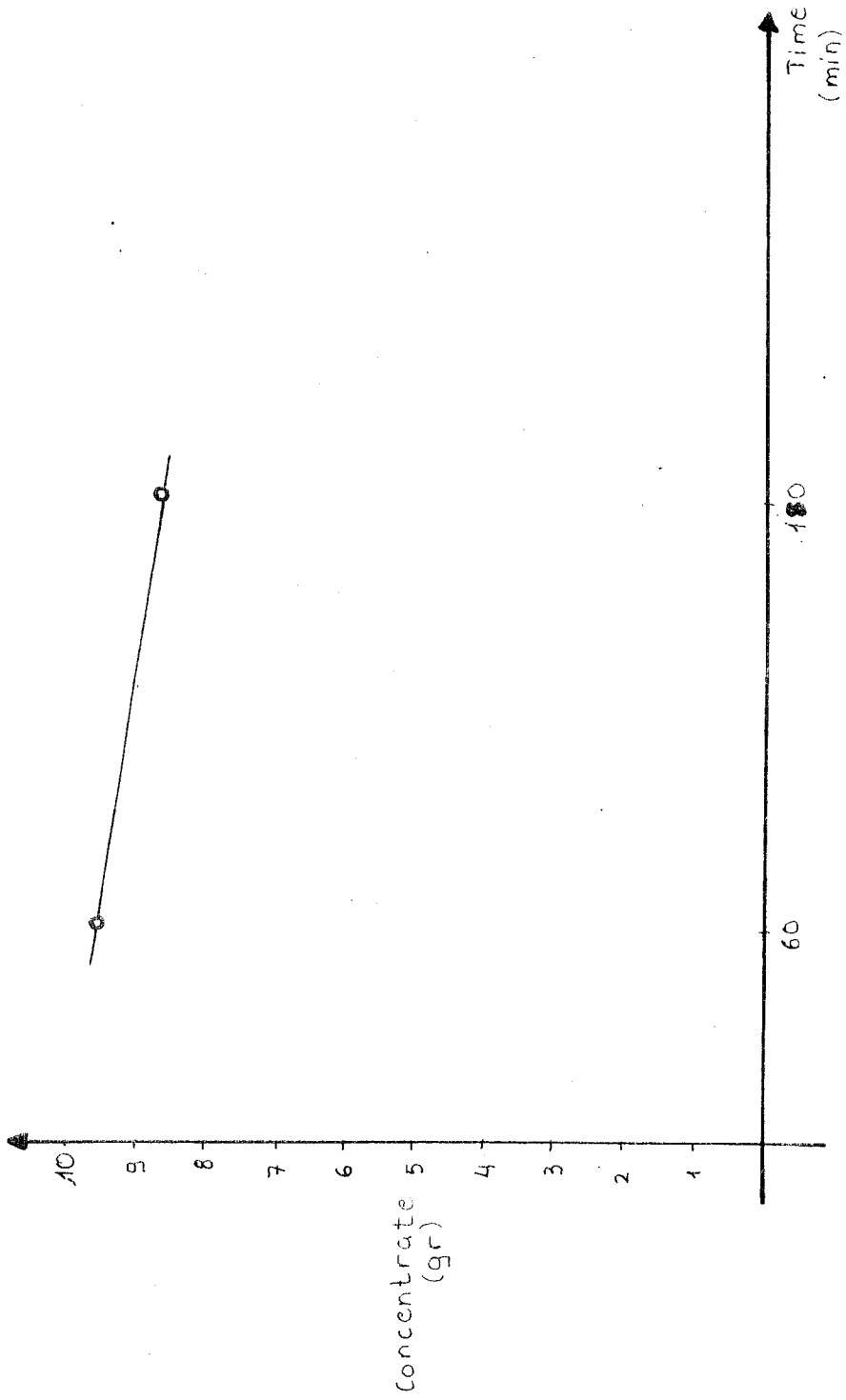
Fig. 7.7- The change of concentrate amount as a function of conditioning time (Flotation time 5 minutes).
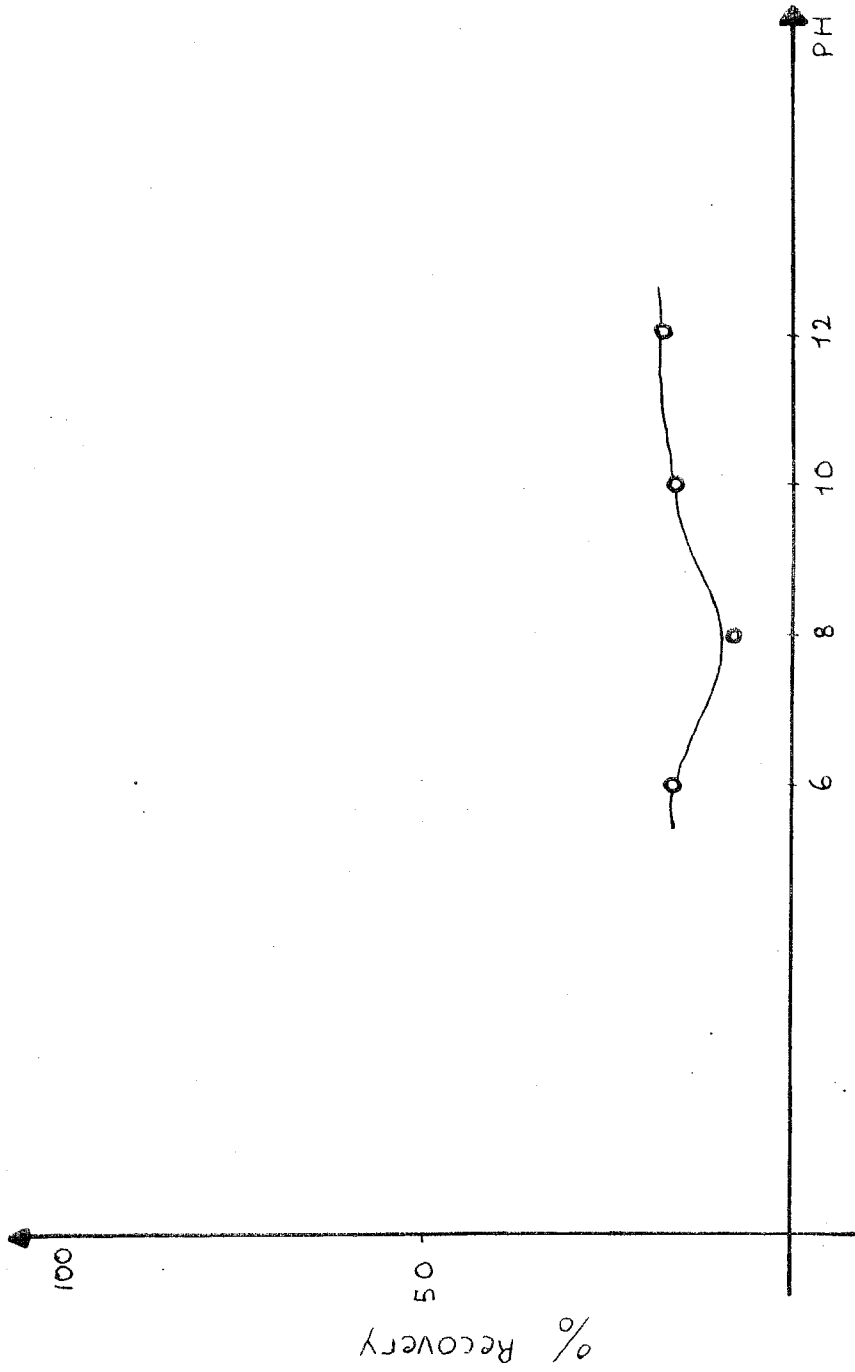
Fig.7.8- The change of Recovery as a function of pH.
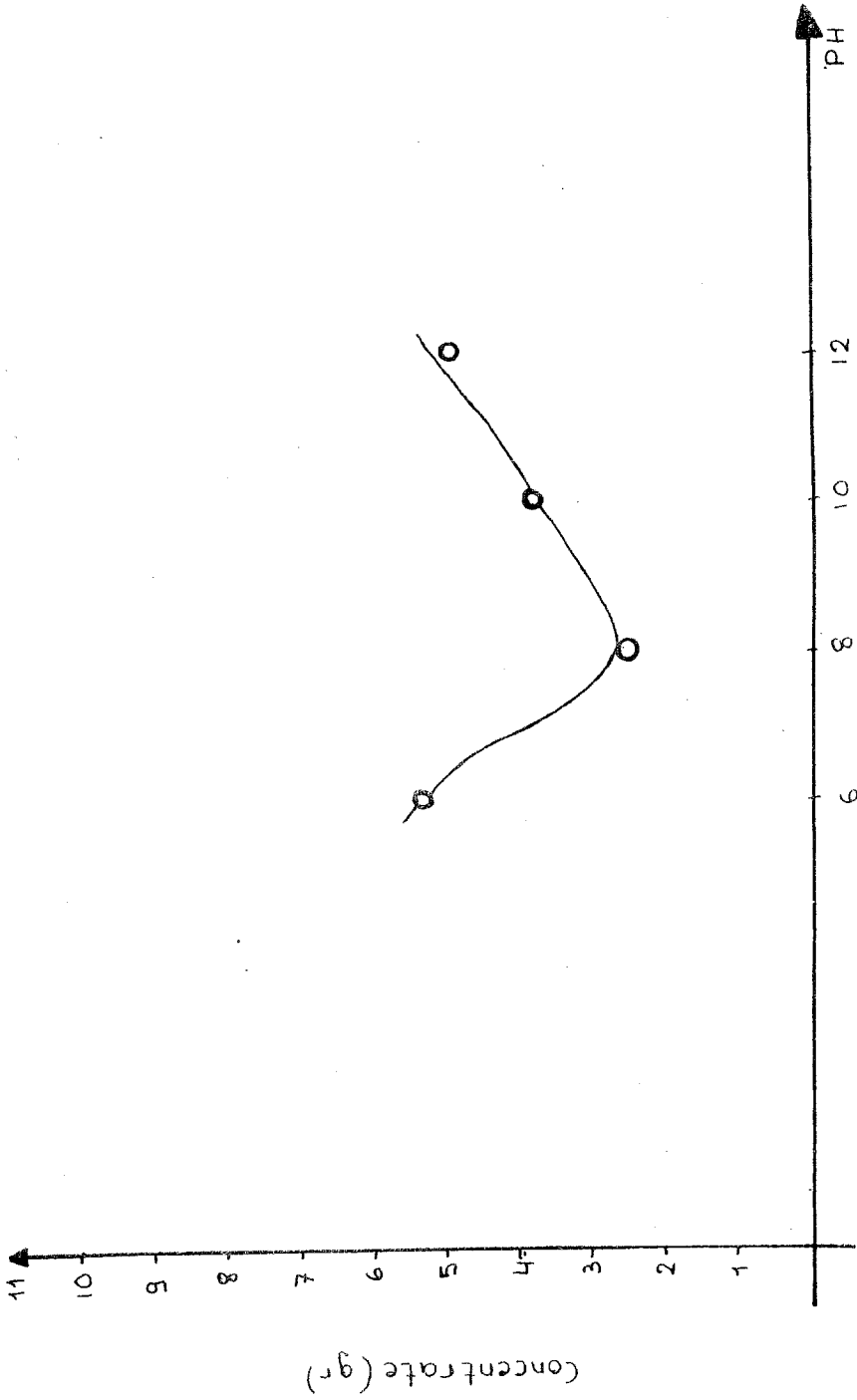
Fig.7.9- The change of concentrate amount as a function of pH.

CHAPTER 8

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

8.A. CONCLUSIONS

The combustion experiments showed that the sample does not contain any material that could burn easily, which is desired to lower the weight of the sediment before the production step. Since the sediment is rich in carbonate content the only way to reduce its weight is by calcining it over $1000^{o}C$. But this process is not a practical solution since energy must be employed to heat the sediment above $1000^{o}C$.

The results of the flotation experiments showed that fatty acid and aryl dithiophosphoric acid promoters of the anionic type and amine promoters of the cationic type found to be the most suitable.

The amounts of the reagents (promoters, activators, depressers) were also changed from the lowest limit as indicated in table 6.13 above the upper limit, but this did not effect the recovery considerably. For this reason it is better to remain below the upper limit for reagent quantities, besides another point is that, large amounts of reagents effect the level of recovery negatively (TA 45).

The best conditions for a high was obtained for froth collecting time of 5 minutes and conditioning time of 60 minutes. While pH of the medium remained about 10 and pulp density was taken as 20%.

The uranium content of the sediment varied from 1.25 ppm up to 12.5 ppm. This shows about 150% enrichment. This value was reached with the conditions of the third experiment on Table 7.2, which also yields the highest recovery among the 20 experiments.

8.B. SUGGESTIONS FOR FURTHER WORK

The suggestions for further work can be classified as follows.

i) The particle size distribution of the sediment and the distribution of uranium is necessary to observe if uranium is concentrated on a particular size range. If this is the case, a physical pre-separation of most of the gangue could be achieved by this way using screening.

ii) Petrographic or metal microscopes are necessary to observe whether a liberation of uranium minerals is attained or not.

iii) Crystallographic or x-ray analysis is necessary to determine the nature of the sediment suitable for flotation purposes.

iv) The sample that was used in this study was too close to the shore so that its uranium and organic material content was probably below the reported limits (DE 77)(3). In the continuation of this study it will be more proper to work on samples taken from middle parts of the Black Sea.

v) In this study 1 cm cells were used for spectrophoto-
metric measurements. Although a desirable sensitivity
was obtained, the use of 10 cm. Cells could be more effective
to increase the sensitivity.

vi) The uranium content of the sediments is not rich
enough to meet the expenses needed for the transport-
ation of the sediment from the bottom to the surface. Besides
mining of such low grade ores may cause important environmental
hazards (DE 77), and it is necessary to find a solution to
these problems. A solution toward economic feasibility could
be the taking of other valuable elements such as Th, Zr, V
etc in to consideration together with uranium. Also, since
the sediments are rich in clay material, after the separation
of these valuable elements it could be used as raw material
in cement production.

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A P P E N D I X

THE CALCULATION OF STANDARD DEVIATION OF CALIBRATION CURVES

To calculate the standard deviation of the points obtained during analytical experiments made for the formation of calibration curves, least squares approximation was applied. Then the variance was calculated and standard deviation was found by taking the square root of the variance.

THE METHOD OF LEAST SQUARE APPROXIMATION

The data obtained during the experiments showed that the relationship between the variables could be represented in a linear fashion. The general analytical expression of a straight line is

$$y = ax + b$$
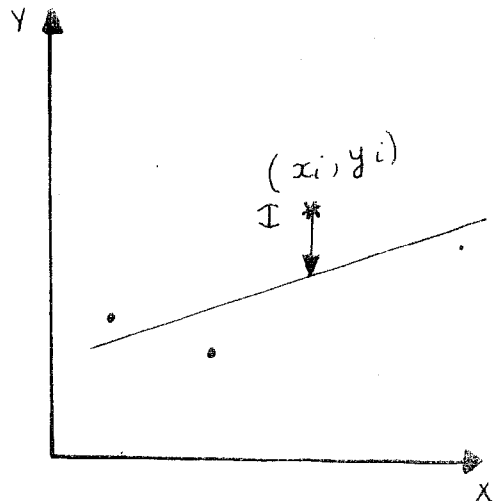
Fig.AP-1- An illustration to show least square approximation.

Assuming a distribution of the data points as shown on the figure (AP 1) and the line approximating the data as closely as possible there will be deviations between the data points and the line. Considering an experimental point $I(x_i, y_i)$, the difference between y_i and y is $y_i - y$ and denotes e between the value suggested by the line and the experimental result.

Therefore if the summation of the squares of these errors can be minimized to obtain the best fitting line. This is accomplished by a proper choice of the parameters a and b.

The error, e, of a point I is

$$e_i = Y_i - y_i \text{ where } Y_i \text{ is the experimental point and}$$
$$y_i \text{ is a point on the line.}$$

The summation of the squares of these errors is

$$S = e_1^2 + e_2^2 + \ldots + e_i^2 + \ldots + e_N^2$$
$$= \sum_{i=1}^{N} e_i^2$$
$$\sum_{i=1}^{N} (Y_i - ax_i - b)^2$$

Here N is the number of data points, and a and b appear as the variables of the problem. In order to minimize S with respect to a and b the two partial derivatives of S, namely, $\partial S / \partial a$ and $\partial S / \partial b$ must both be set equal to zero.

$$\frac{\partial S}{\partial a} = 0 = \sum_{i=1}^{N} 2(Y_i - ax_i - b)(-x_i)$$

$$\frac{\partial S}{\partial b} = 0 = \sum_{i=1}^{N} 2(Y_i - ax_i - b)(-1)$$

$$a\Sigma x_i^2 + b\Sigma x_i = \Sigma x_i Y_i$$

$$a\Sigma x_i + bN = \Sigma Y_i \qquad i = 1 \ldots N.$$

a and b are solved from these equations as;

$$a = \frac{(\Sigma x_i)(\Sigma y_i) - N\Sigma x_i y_i}{(\Sigma x_i)^2 - N\Sigma x_i^2}$$

$$b = \frac{(\Sigma x_i) \cdot (\Sigma x_i y_i) - (\Sigma x_i)(\Sigma y_i)}{(\Sigma x_i)^2 - N\Sigma x_i^2}$$

STANDARD DEVIATION OF THE EXPERIMENTAL POINTS

After the expression for the least squares line is found the variance of the data points is calculated by the following formula (GE 78)

$$\sigma^2 = \frac{\Sigma e_i^2}{N-n-1}$$

Where N is number of data points

n degree of the polynomial approximating the data which is 1 for the linear curve fitting

e_i is the error as indicated above.

Since the standard deviation is the positive square root of the variance it is given by

$$S_D = \sigma = \sqrt{\sigma^2}.$$

The relevant calculations are made through the use of the following computer programs. .

FIG.5-1

```
      PROGRAM SELIM
      CALCULATION OF STANDARD DEVIATION FOR THE POINTS ON
      DIMENSION X(10),Y(10),Y1(10),E(10)
    5 READ(5,1)(X(I),Y(I),I=1,N)
      READ(5,2)(X(I),Y(I),I=1,N)
    1 FORMAT(2F7.5)
   10 WRITE(6,20)
   20 FORMAT(20X,'INPUT DATA',//)

      WRITE(6,21)
   21 FORMAT(20X,'CONSTANTS',//)
      WRITE(6,24)A,B
   24 FORMAT(20X,'A=',F10.5,10X,'B=',F10.5)
   55 WRITE(6,25)
   25 FORMAT(20X,'ERRORS',//)

   60 WRITE(6,26)
   26 FORMAT(20X,'STANDARD DEVIATION',//)
   75 WRITE(6,27)STDEV
   80 FORMAT(20X,'STDEV=',F10.5)
      END
```

ENTERING USER PROGRAM

INPUT DATA

```
0.0000     0.0000
0.0000     0.0000
0.0000     0.0000
0.4084     0.0000
0.4140     0.0000
```

```
 .96000    .27300
1.28000    .34400
```

CONSTANTS

A= .27254   B= .00984

ERRORS

```
ER 1 =
ER 2 =
ER 3 =
ER 4 =
ER 5 =
ER 6 =
ER 7 =
```

STANDARD DEVIATION

STDV= .01219

```
      PROGRAM BEHAR(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
C     CALCULATION OF STANDARD DEVIATION FOR THE POINTS ON FIG. 6-2
      DIMENSION X(10),Y(10),Y1(10),E(10)

      READ(5,5) N
    5 FORMAT(I2)
      READ(5,50) (X(I),Y(I),I=1,N)
   50 FORMAT(2X,7.5)
      WRITE(6,20) (X(I),Y(I),I=1,N)
   20 FORMAT(//,' INPUT DATA',//)

...

      WRITE(6,20) AA,BB
   40 FORMAT(//,' CONSTANTS',//,F10.5,10X,'B=',F10.5,//)

...

      WRITE(6,55) (E(I),I=1,N)
   55 FORMAT(//,' ERRORS',//)

      WRITE(6,60) VAR
   65 FORMAT(//,' STANDARD DEVIATION',//)
      WRITE(6,) STDV,F10.5

      END
```

ENTERING USER PROGRAM

INPUT DATA

```
.03000   .01700
.03000   .05000
.03000   .17000
.03000   .45000
.03000   .62000
```

1.90000   .58600

CONSTANTS

A= .30929   B= -.00178

ERRORS

```
.01000   -.07001
.02000   -.03207
.03000   -.07237
.04000   -.01507
.05000   -.00007
.06000   -.00007
```

STANDARD DEVIATION

STDV= .90601

FIG. 6-3

```
WRITE(5,10)X(I),Y(I),Y1(I0),E(10)
FORMAT(5H ... STANDARD DEVIATION FOR THE POINTS ON FIG. 6-3
WRITE(5,11)(X(I),Y(I),I=1,N)
WRITE(5,12)(X(I),Y(I),I=1,N)
FORMAT(   INPUT DATA,//)

FORMAT(20X, CONSTANTS,//)
FORMAT(   A=,F10.5,10X,BE=,F10.5,//)
FORMAT(20X, ERRORS,//)

FORMAT(   STANDARD DEVIATION,//)
FORMAT(   DEV,F10.5)
```

INPUT DATA

14.32000   .13200

CONSTANTS

A=   .00834   B=   .01258

ERRORS

STANDARD DEVIATION

STDV=   .00682

```
C      CALCULATION OF STANDARD DEVIATION FOR THE POINTS ON FIG. 6-4
       REAL STD,Y(10),Y(10),YL(10),YL(10),LE(10)
       ...
    5  READ(5,5)(X(I),Y(I),I=1,N))
       FORMAT(E7,5)
       READ(6,15)(X(I),Y(I),I=1,N)
       FORMAT(//, INPUT DATA,//)
       WRITE(6,20)
       FORMAT(20X,2E10.5)
       ...
   10  DO 10 J=1,N
       RR=RR+Y(J)
       RB=RB+Y(J)
       AA=AA+X(J)
       CC=CC+X(J)**2
   10  CONTINUE
       DMB=RB*C-AA*AN
       A=(RR+C+AA)/DMB
       B=(CC+AA+B)/DMB
       WRITE(6,25)A,B
       FORMAT(//,20X, CONSTANTS,//)
       FORMAT(6,25)A=,AE,,F10.5,10X,B=,BE,,F10.5)
       WRITE(6,55)
       FORMAT(//,20X, ERRORS,//)
       DO 50 I=1,N
       Y=L(I)=A+X(I)+B
   60  DY=L(I)=Y(I)-YL(I)
       FORMAT(6,60)
       FORMAT(5,60X,E(I+10+)E,,F10.5)
   50  CONTINUE
       VAR=SQRT(V/(N-1))
       STDV=SQRT(VAR)
       WRITE(6,70)STDV
       FORMAT(//,20X, STANDARD DEVIATION,//)
       FORMAT(6,80)STDV
       FORMAT(20X, STDV=,F10.5)
       STOP
       END
```

ENTERING USER PROGRAM

INPUT DATA

```
1.500000      .00000
2.030000      .02000
5.700000      .05000
8.060000      .06000
12.050000     .11000
```

```
15.82000      .13200
```

CONSTANTS

A= .00934   B= .00006

ERRORS

```
E1    .00353
E2    .00447
E3    .00552
E4    .00346
E5    .00368
E6    .00069
```

STANDARD DEVIATION

STDV= .00632