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**EUROPEAN ATOMIC ENERGY COMMUNITY - EURATOM**

**CHEMICAL ANALYSIS OF PLUTONIUM BEARING  
NON-IRRADIATED FUELS AND THEIR COMPONENTS**

by

**M.J. MAURICE, L.M. ANGELETTI and K. BUIJS**

**1969**



**Joint Nuclear Research Center  
Karlsruhe Establishment - Germany  
European Transuranium Institute**



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A scheme for the analysis of plutonium containing nuclear fuels and their components is presented and detailed procedures are given.

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A scheme for the analysis of plutonium containing nuclear fuels and their components is presented and detailed procedures are given.

1. The first part of the document discusses the importance of maintaining accurate records of all transactions. It emphasizes that this is crucial for ensuring the integrity of the financial statements and for providing a clear audit trail. The text also mentions that proper record-keeping is essential for identifying and correcting errors in a timely manner.

2. The second part of the document focuses on the role of internal controls in preventing fraud and misstatements. It highlights that a strong internal control system is necessary to ensure that all transactions are properly authorized, recorded, and reviewed. The text also notes that internal controls should be designed to be effective and efficient, and should be regularly evaluated and updated as needed.

3. The third part of the document discusses the importance of transparency and communication in financial reporting. It emphasizes that providing clear and concise information to stakeholders is essential for building trust and confidence in the organization's financial performance. The text also mentions that transparency is a key component of corporate governance and is necessary for ensuring the long-term success of the organization.

4. The fourth part of the document discusses the importance of compliance with applicable laws and regulations. It emphasizes that organizations must ensure that their financial reporting practices are in full compliance with all relevant laws and regulations. The text also mentions that compliance is a key component of risk management and is necessary for avoiding legal and financial penalties.

5. The fifth part of the document discusses the importance of continuous improvement in financial reporting. It emphasizes that organizations should regularly evaluate their financial reporting processes and make improvements as needed. The text also mentions that continuous improvement is a key component of quality management and is necessary for ensuring the highest quality of financial reporting.

6. The sixth part of the document discusses the importance of ethical behavior in financial reporting. It emphasizes that organizations should always act ethically and with integrity in all financial reporting activities. The text also mentions that ethical behavior is a key component of corporate governance and is necessary for ensuring the long-term success of the organization.

7. The seventh part of the document discusses the importance of stakeholder engagement in financial reporting. It emphasizes that organizations should actively engage with their stakeholders and listen to their concerns. The text also mentions that stakeholder engagement is a key component of corporate governance and is necessary for ensuring that the organization's financial reporting practices are in line with the expectations of its stakeholders.

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## **ABSTRACT**

A scheme for the analysis of plutonium containing nuclear fuels and their components is presented and detailed procedures are given.

## **KEYWORDS**

CHEMICAL ANALYSIS  
PLUTONIUM  
~~STAINING~~  
FUELS

## PART A

GENERAL REMARKS

1. Introduction
2. Scheme of analysis and survey of methods
3. Dissolution of samples
4. Emission spectrographic analysis
5. References

ACKNOWLEDGEMENT

The authors wish to thank all those who collaborated in the development of the described methods and more particularly Messrs W.J. Bartscher, B. Chavane de Dalmassy and W. Hecq.



## 1. INTRODUCTION (\*)

In the present report a number of chemical methods for the analysis of non-irradiated nuclear fuels and their components is given. The components involved are plutonium, uranium, plutonium- and uranium oxide, - carbide and - nitride, whereas the fuels dealt with are plutonium-uranium alloys, plutonium- uranium oxides, - carbides and- nitrides.

The methods given are applied in our Institute on a routine basis. The large numbers of results obtained in the period 1965-1969 make it possible to judge well their precision, accuracy, limit of detection and sensitivity to interferences.

The determination of gases will not be dealt with: this subject will be discussed in a separate paper.

## 2. SCHEME OF ANALYSIS; SURVEY OF METHODS

A scheme for the analysis of the fuels and their components is given in fig. 1, where the sample preparations and the properties to be determined are indicated. A survey of methods to determine these properties starting from prepared samples, is given in table 1. Detailed procedures are given in part B of this report.

In table 1 the precision is given as the standard deviation of a single determination for the scope mentioned. When the standard deviation cannot be used as a measure for the precision as e.g. in the emission spectrographic analysis, the coefficient of variation is used. This is indicated in the column "precision". It should be noted that the indicated standard deviations apply to the samples described in the scope, i.e. in the case of the plutonium determination the standard deviation of 0,030 mg is found when plutonium is determined in an aqueous solution. This

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(\*) Manuscript received on 14 April 1969.

value is not valid any more when plutonium is determined in a mixed plutonium-uranium oxide pellet. The pellet must be dissolved which contributes also to the precision of the final result. This is shown clearly by an analysis of variance of a large number of results of plutonium and uranium determinations in mixed oxides (15% - 85%). In this analysis the following values for the standard deviations and coefficients of variation were found (table 2).

Table 2

source of variation	plutonium			uranium		
	st.dev. in mg	st.dev. in %Pu	coeff. of var.	st.dev. in mg	st.dev. in %Pu	coeff. of var.
analysis	0.030	0.015	0.11%	0.058	0.058	0.08
analysis + dissolution	0.092	0.046	0.35	0.15	0.15	0.20

It follows from table 2 that under the conditions of the determinations the coefficient of variation of a single determination of the uranium to plutonium ratio is 0.4%. The standard deviations given in table 1 include the contributions of blanks.

The limit of detection is defined as 3.29 times the standard deviation (5.1.)

Some of the methods are dependent methods, i.e. the accuracy of the results depends upon the accuracy of the method used for calibration. An example is the spectrophotometric determination of traces of plutonium, where the accuracy depends upon the accuracy of the method used to determine the purity of the sample used for calibration. For these dependent methods the way of calibration is indicated in the column "accuracy". For the other - independent - methods agreement between the results obtained and those found with another independent method is indicated in this column.



In the next columns the standardization, the interferences and the applications are listed. The numbers indicated in the column "procedure" refer to part B of this report.

### 3. DISSOLUTION OF SAMPLES

Metals, alloys and nitrides are rapidly dissolved in a mixture of nitric acid and hydrofluoric acid. High-fired plutonium oxide and plutonium-uranium oxides in the form of incomplete solid solutions are very difficult to dissolve in this solvent. To overcome this difficulty we adopted a fusion method : the sample is fused with a mixture of potassium pyrosulphate and sodium pyrosulphate (1 + 4) and the melt is dissolved in nitric acid. The whole operation takes about 30 min. In this method the use of nitric acid is indispensable to dissolve the melt. Therefore, the method cannot be used in cases where nitrate interferes with the subsequent plutonium and/or uranium determination as e.g. in the coulometric determination of plutonium and uranium. For these cases another dissolution method was developed: the sample is boiled with sulphuric acid, nitric acid and ammonium sulphate and finally heated to fuming to eliminate quantitatively nitrate and to complete dissolution. The solution obtained is diluted with water. The preparation of such a solution takes about 40 min.

When carbides are dissolved in nitric or sulphuric acid the solution obtained may contain free carbon and organic compounds formed in the decomposition of the carbide. These compounds may interfere with the cerimetric plutonium determination and with the coulometric method. It was, therefore, decided to eliminate carbon quantitatively from the sample by calcination prior to dissolution. Since this calcination has to be carried out at a relatively high temperature it is preferable to apply either the fusion method or the dissolution in sulphuric acid, nitric acid and ammonium sulphate to dissolve the oxide obtained.

#### 4. EMISSION SPECTROGRAPHIC ANALYSIS

For the determination of trace impurities the carrier distillation method (5.2.) was adopted. Cobalt oxide is used as an internal standard. Prior to analysis samples to be analysed are converted into plutonium oxide, triuranium octoxide or a mixture of these. In order to account for matrix influences calibration graphs were drawn up using the following different types of standards :

- a) triuranium octoxide samples no 95 (1-7), obtained from the National Bureau of Standards, Washington, U.S.A. Calibration graphs prepared with these samples are used in the analysis of pure uranium oxide samples and uranium oxides containing small amounts of plutonium;
- b) plutonium oxide samples, prepared by repeated anion exchange of a solution of plutonium nitrate in 7 M nitric acid, followed by repeated precipitation as plutonium oxalate, calcination and addition of known amounts of the trace impurities. Calibration graphs prepared with these samples are used in the analysis of plutonium oxide;
- c) a mixture of 85 parts of the samples mentioned under a) and 15 parts of the samples mentioned under b). These calibration graphs are used in the analysis of plutonium-uranium oxides containing 10 to 20% plutonium.



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PART B                    PROCEDURES1.            BASIC INSTRUCTIONS

- 1.1.           Cerimetric determination of plutonium with constant current potentiometric detection of the end point
- 1.2.           Spectrophotometric determination of plutonium
- 1.3.           Oxidimetric determination of uranium
- 1.4.           Controlled potential coulometric determination of plutonium and uranium
- 1.5.           Standardization of cerium (IV) sulphate solution

2.            THE DETERMINATION OF PLUTONIUM AND URANIUM IN FUELS AND THEIR COMPONENTS. PROCEDURES FOR DISSOLUTION AND FUSION OF SAMPLES

- 2.1.           Determination of plutonium and/or uranium in plutonium metal, uranium metal, plutonium-uranium alloys, plutonium nitride, plutonium-uranium nitrides and plutonium-uranium oxides
- 2.2.           Determination of plutonium and/or uranium in plutonium oxide and plutonium-uranium oxides
- 2.3.           Determination of plutonium and/or uranium in plutonium carbide, uranium carbide and plutonium-uranium carbides
- 2.4.           Determination of uranium in uranium nitride and uranium oxide



3. PROCEDURES FOR THE DIRECT ANALYSIS OF FUELS AND THEIR COMPONENTS

- 3.1. Determination of carbon in plutonium metal, uranium metal, plutonium-uranium alloys, plutonium oxide, uranium oxide, plutonium-uranium oxides, plutonium carbide, uranium carbide, plutonium-uranium carbides, plutonium nitride, uranium nitride and plutonium-uranium nitrides
- 3.2. Gravimetric determination of the oxygen to metal ratio in plutonium oxide, uranium oxide and plutonium-uranium oxides
- 3.3. Coulometric determination of the oxygen to metal ratio in uranium oxide
- 3.4. Coulometric determination of traces of water in plutonium oxide, uranium oxide and plutonium-uranium oxides
- 3.5. Emission spectrographic determination of traces of metals in plutonium metal, uranium metal, plutonium-uranium alloys, plutonium nitride, uranium nitride, plutonium-uranium nitrides, plutonium carbide, uranium carbide, plutonium-uranium carbides, plutonium oxide, uranium oxide and plutonium-uranium oxides.

1. BASIC INSTRUCTIONS1.1. Cerimetric determination of plutonium with constant current potentiometric detection of the end point1.1.1. Scope

The method is applicable to the determination of from 1 to 50 mg of plutonium in at maximum 50 ml of aqueous solution which is at least 1 N in nitric acid or sulphuric acid. Chloride, bromide, iodide and thiocyanate interfere and must be removed previously. Chromium, manganese, cerium, vanadium and tungsten interfere. Uranium does not interfere.

1.1.2. Principle

Plutonium is oxidized to plutonium (VI) by means of silver (II) oxide and subsequently reduced by a known amount of iron (II) after destruction of the excess of silver (II). The excess of iron (II) is titrated with a cerium (IV) sulphate solution, the end-point being detected by constant current potentiometry.

1.1.3. Apparatus

- a) 1 double platinum electrode
- b) 1 apparatus to maintain a constant current of 3 - 5  $\mu$ A between the platinum electrodes. It is advantageous to use a piston burette connected to a mV recorder. A much simpler apparatus can be constructed according to fig. 2.

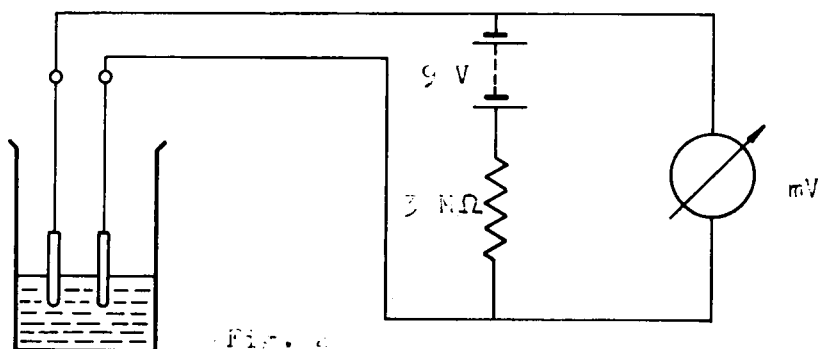


Fig. 2

- c) 1 100-ml beaker
- d) 1 10-ml measuring pipette
- e) 1 20-ml pipette
- f) 1 50-ml burette or a piston burette

1.1.4. Reagents

- a) Nitric acid, 2 M. : dilute 50 ml of concentrated nitric acid ( $d=1.40$ ) with water to 350 ml.
- b) Silver (II) oxide : dissolve 72 g of sodium hydroxide in 1000 ml of water at about  $85^{\circ}$  C. Add 75 g of potassium persulphate and 51 g of silver nitrate previously dissolved in 15 to 20 ml of water. The temperature of the solution increases to about  $90^{\circ}$  C. Stir carefully for 15 minutes. A black precipitate of silver (II) oxide is then formed. Filter over a buchner funnel. Wash the precipitate with a very dilute solution of sodium hydroxide in order to eliminate sulphate ions. Dry in air.
- c) Sulphamic acid solution : dissolve 9.7 g of sulphamic acid in water and dilute to 100 ml.
- d) Aluminium nitrate solution : dissolve 37.5 g of aluminium nitrate nanohydrate in water and dilute with water to 1 l.
- e) Iron (II) sulphate solution : dissolve 14 g of iron (II) sulphate heptahydrate in water, add 27 ml of concentrated sulphuric acid and dilute with water to 2 l.
- f) Cerium (IV) sulphate solution, 0.01 (t) N: add 270 ml of concentrated sulphuric acid to 40.4 g of cerium (IV) sulphate tetrahydrate. Add water carefully and dissolve the salt. Dilute with water to 10 l. Standardize the solution according to procedure 1.5. and store it in a colourless glass bottle.

1.1.5. Sample

At maximum 50 ml of an aqueous solution of plutonium nitrate or sulphate which is at least 1 N in nitric acid or sulphuric acid and contains 1 to 50 mg of plutonium.

1.1.6. Procedure

Transfer the sample into a 100-ml beaker. Add 5 ml of 2 M nitric acid and then 100 mg of silver (II) oxide. Swirl the solution from time to time for 15 minutes and heat to



boiling. Keep the solution at a temperature near the boiling point for 5 minutes and then cool. Add 1 ml of sulphamic acid solution (see 1.1.8.1.) and 2 ml of aluminium nitrate solution (see 1.1.8.2.). Next, add by pipette 20 ml of iron (II) sulphate solution. After 5 minutes insert the electrode into the solution and titrate the excess of iron (II) with 0.01 (t)N cerium (IV) sulphate solution, maintaining a constant current of  $3\mu\text{A}$  between the electrodes. Record the potential as a function of the amount of cerium (IV) solution added. Determine the equivalence point from the titration curve ( $v_1$  ml consumed). Carry out a blanc on 20 ml of the iron (II) sulphate solution ( $v_2$  ml consumed).

#### 1.1.7. Calculation

The sample contains

$$A = (v_2 - v_1) t \times EW_{\text{Pu}} \text{ mg of plutonium}$$

where  $EW_{\text{Pu}}$  = equivalent weight of plutonium (see 1.1.8.3.).

Report the result to the nearest 0.01 mg

#### 1.1.8. Remarks

1.1.8.1. Sulphamic acid is added to avoid oxidation of iron (II) by nitrous acid.

1.1.8.2. Aluminium nitrate is added in order to mask fluoride. In the absence of fluoride this addition can be omitted.

1.1.8.3. The equivalent weight varies with isotopic composition. For  $x\%$  of  $^{240}\text{Pu}$  and  $(100 - x)\%$  of  $^{239}\text{Pu}$  the equivalent weight is equal to

$$\frac{240.05 x + (100 - x) 239.05}{200}$$

200

## 1.2. Spectrophotometric determination of plutonium

### 1.2.1. Scope

The method is applicable to the determination of from 0.02 to 7 mg of plutonium in at maximum 40 ml of aqueous solution. 1.6 mmoles of phosphate, 5 mmoles of sulphate, 2 mmoles of fluoride, 1000 mg of uranium, 350 mg of cerium, 5 mg of manganese and at least 15 mg of thorium, aluminium, cobalt, chromium, iron, molybdenum, nickel, vanadium and zirconium do not interfere. Chloride, bromide and iodide interfere (see 1.2.9.1.)

### 1.2.2. Principle

Plutonium is oxidized to the hexavalent state in 4 M nitric acid with silver (II) oxide and its absorbance is measured at 831 nm.

### 1.2.3. Apparatus

- a) A recording spectrophotometer provided with scale expansion, readable slit width and 10 cm-cells, e.g. Beckman DK-2A
- b) 1 100-ml beaker
- c) 1 50-ml volumetric flask.

### 1.2.4. Reagents

- a) Nitric acid, 14 M
- b) Silver (II) oxide, prepared according to procedure 1.1. sect. 1.1.4. b.

### 1.2.5. Sample

At maximum 40 ml of an aqueous plutonium solution.

1.2.6. Procedure

Transfer the sample to a 100-ml beaker and make the solution 4 M in nitric acid, either by addition of 14 M nitric acid or by dilution, taking care that the final volume does not exceed 40 ml. Add under stirring so much silver (II) oxide that a black colour persists for 5 min. After 5 min heat slowly to near boiling until the colour has disappeared. Cool, transfer to a 50-ml volumetric flask, and make up to volume with 4 M nitric acid. Record the absorption spectrum of this solution from 750 to 900 nm in a 10 cm cell against 4 M nitric acid as a blank. Read the slit width at the moment at which the recorder indicates the maximum of the absorption peak. Construct the base line on the recorded spectrum and measure the difference in absorbance between the peak maximum and the corresponding background. In the case that scale expansion is used, convert the transmission values measured into absorbance values before making the background correction. From the plutonium absorbance thus determined and the measured slit width determine the plutonium quantity with the aid of an equation, relating absorbance to plutonium concentration and slit width. (A' mg of plutonium found).

1.2.7. Calculation

The sample contains:  $\frac{A'}{v}$  g/l where v = volume of the sample.  
 Report the results to the nearest  $\frac{0.002}{v}$  g/l for amounts smaller than  $\frac{0.5}{v}$  g/l and to the nearest  $\frac{0.0045 A'}{v}$  g/l for amounts from  $\frac{0.5}{v}$  to  $\frac{7}{v}$  g/l.

1.2.8. Calibration equation

Dissolve about 200 (p) mg of plutonium metal of guaranteed purity (e.g. sample 949 b of the National Bureau of Standards, Washington D.C. - USA) in about 10 M nitric acid and dilute with nitric acid to 1 l so as to obtain a final



solution which is 4 M in nitric acid. This solution contains p mg of plutonium per l. Pipette 5, 10, 15, 20, 25, 30 and 35 ml of this solution in 100-ml beakers and follow the procedure described above. Measure the absorbances of these solutions at different slit widths. Calculate the equation relating the absorbance to plutonium concentration and slit width according to the method of the least squares.

1.2.9. Remarks

- 1.2.9.1. When chloride, bromide or iodide are present, the precipitate left after the destruction of excess silver (II) must be eliminated by centrifuging.

### 1.3. Oxidimetric determination of uranium

#### 1.3.1. Scope

The method is applicable to the determination of from 2 to 300 mg of uranium in at maximum 15 ml of aqueous solution that contains no more than 50 mmols of nitrate and 1 mg of molybdenum. Plutonium and iron do not interfere.

#### 1.3.2. Principle

Uranium (VI) is reduced to uranium (IV) in a concentrated phosphoric acid solution containing sulphamic acid by an excess of iron (II) sulphate. The excess of iron (II) is subsequently oxidized by nitric acid in the presence of molybdenum (VI) as a catalyst and uranium (IV) is titrated with standard potassium dichromate solution using barium diphenylamine sulphonate as an indicator.

#### 1.3.3. Apparatus

- a) 1 750-ml conical flask
- b) 1 5-ml pipette
- c) 2 50-ml measuring cylinders
- d) 2,5-ml measuring pipettes
- e) 1 200-ml measuring cylinder
- f) 1 50-ml burette
- g) 2 2-ml pipettes
- h) 1 1-ml pipette

1.3.4. Reagents

- a) Sulphamic acid solution: dissolve 150 g of sulphamic acid in water and dilute with water to 1 l.
- b) Phosphoric acid, concentrated, spec. grav. 1.75.
- c) Iron (II) sulphate solution, 1 M: add carefully under constant shaking 100 ml of concentrated sulphuric acid to 750 ml of water. Add 280 g of iron (II) sulphate heptahydrate to the hot solution and shake until dissolution is complete. Dilute with water to 1 l.
- d) Nitric acid-sulphamic acid mixture: dilute 250 ml of concentrated nitric acid to 930 ml with water. Shake and add 70 ml of 1.5 M sulphamic acid solution.
- e) Ammonium molybdate solution, 1 %: dissolve 10 g of ammonium heptamolybdate ( $(\text{NH}_4)_6 \text{Mo}_7 \text{O}_{24} \cdot 4\text{H}_2\text{O}$ ) in about 250 ml of hot water. Cool, dilute with water to 1 l and mix.
- f) Sulphuric acid, 9 M: carefully add concentrated sulphuric acid to an equal volume of water, cool and mix.
- g) Barium diphenylamine sulphonate solution, 0.04 %: dissolve 0.2 g of barium diphenylamine sulphonate in boiling water, cool, dilute with water to 500 ml and mix.
- h) Potassium dichromate solution, 0.05 (t) N: weigh out to the nearest 0.1 mg 5 (p)g of potassium dichromate and dilute with water to 2 l. The titre of the solution is  $t = \frac{P}{98.063}$
- i) Iron (II) ammonium sulphate solution, 0.01 M: dissolve 3.95 g of iron (II) ammonium sulphate hexahydrate in water and dilute to 1 l.
- j) Nitric acid, 10 M: dilute 100 ml of concentrated nitric acid with water to 140 ml.

1.3.5. Sample

At maximum 15 ml of an aqueous solution containing from 2 to 300 mg of uranium and no more than 50 mmoles of nitrate.



1.3.6. Procedure

Transfer the sample to a 750-ml conical flask and add 5 ml of 10 M nitric acid and 5 ml of sulphamic acid solution. Swirl and add 40 ml of concentrated phosphoric acid. Swirl and add by pipette 5 ml of 1 M iron (II) sulphate solution. Take care that not any drop of this solution remains on the wall of the flask. Swirl and add 5 ml of the nitric acid-sulphamic acid mixture. Swirl again and add 2 ml of ammonium molybdate solution. Shake and wait until the brown colour has disappeared. 5 minutes later add 25 ml of 9 M sulphuric acid and 200 ml of water. Mix well and add 2 ml of barium diphenylamine sulphonate solution. Titrate with 0.05 (t) N potassium dichromate solution until an intense violet colour persists. Add 1 ml of 0.01 M iron (II) ammonium sulphate solution, so that the solution becomes clear green again. Continue the titration until an intense violet persists for 1 minute ( $v_1$  ml consumed). Carry out a blanc in the same way but now take 15 ml of water instead of sample ( $v_2$  ml consumed).

1.3.7. Calculation

The sample contains

$$B = (v_1 - v_2) \cdot EW_U \text{ mg of uranium}$$

where  $EW_U$  = equivalent weight of uranium (see 1.3.8.3.)

Report the results to the nearest 0.02 mg.

1.3.8. Remarks

- 1.3.8.1. After the addition of 200 ml of water the determination should be finished within 10 minutes.
- 1.3.8.2. When plutonium is present a precipitate may occur after addition of phosphoric acid. This will redissolve during the next operations.

1.3.8.3. The equivalent weight varies with isotopic composition. For  $x$  % of  $^{235}$  uranium and  $(100 - x)$ % of  $^{238}$  uranium the equivalent weight is equal to

$$\frac{235,04 x + (100 - x) 238,05}{200}$$

1.4. Controlled potential coulometric determination of plutonium and uranium

1.4.1. Scope

The method is applicable to the determination of from 0.2 to 25 mg of plutonium (IV) and of from 0.7 to 45 mg of uranium (VI) in at maximum 10 ml of aqueous solution, which does not contain nitrate and chloride. Titanium (IV), iron (III), tungsten (VI), molybdenum (VI), vanadium (V), bismuth (III) and copper (II) interfere (see 1.4.8.).

1.4.2. Principle

After a pre-electrolysis of 0.5 M sulphuric acid on a mercury pool electrode at + 0.1 V vs silver-silver chloride electrode the sample is added to the cell and plutonium (IV) is reduced to the trivalent state. Next, the potential is lowered to - 0.35 V and uranium (VI) is reduced to uranium (IV).

1.4.3. Apparatus

- a) 1 controlled potential coulometer with electronic potentiostat and electronic integrator, provided with a digital voltmeter.
- b) 1 electrolysis cell with a mercury pool electrode, platinum wire helix and silver-silver chloride electrode according to fig. 3
- c) 2 10-ml measuring cylinders.
- d) 1 10-ml pipette.

1.4.4. Reagents

- a) Mercury, distilled twice
- b) Sulphuric acid, 0.5 M: dilute 25 ml of concentrated sulphuric acid with water to 900 ml
- c) Sulphamic acid, solid
- d) Nitrogen, oxygen-free

1.4.5. Sample

At maximum 10 ml of a nitrate- and chloride-free aqueous solution containing of from 0.2 to 25 mg of plutonium in the tetravalent state and of from 0.7 to 45 mg of uranium in the hexavalent state.

1.4.6. Procedure

Transfer to the electrolysis cell 5 ml of mercury, 5 ml of 0.5 M sulphuric acid and 200 mg of sulphamic acid. Pass a stream of nitrogen through the solution and electrolyse at + 0.1 V vs silver-silver chloride electrode until the current has dropped to 30  $\mu$ A. Pass the stream of nitrogen over the solution, add the sample and electrolyse until the residual current has become constant. Measure the quantity of electricity in coulomb which has flown since the addition of the sample ( $Q_1$ ), the residual current ( $i_1$  Amps) and the corresponding electrolysis time ( $t_1$  sec). Set the potential at - 0.35 V and electrolyse as before. Record the quantity of electricity flown ( $Q_2$ ), the residual current ( $i_2$  Amps) and the electrolysis time ( $t_2$  sec). Carry out a blank with all reagents used, including those used in the sample preparation, and follow the sample preparation procedure and the procedure described above. Record the quantities of electricity flown ( $Q_1'$  and  $Q_2'$  respectively), the residual currents ( $i_1'$  and  $i_2'$  respectively) and the electrolysis times ( $t_1'$  and  $t_2'$  respectively).

1.4.7. Calculation

The sample contains :

$$A = \frac{\{(Q_1 - i_1 t_1) - (Q_1' - i_1' t_1')\}}{96.5} EW_{Pu} \text{ mg of plutonium}$$

$$B = \frac{\{(Q_2 - i_2 t_2) - (Q_2' - i_2' t_2')\}}{193} EW_U \text{ mg of uranium}$$

where  $EW_{Pu}$  and  $EW_U$  are the atomic weights of plutonium and uranium respectively.

Report the result to the nearest 0.002 mg for plutonium and to the nearest 0.01 mg for uranium.

1.4.8. Remarks

- 1.4.8.1. The effect of the quantities of interfering elements normally present in plutonium - and uranium compounds may be neglected.
- 1.4.8.2. The interferences of iron (III), and vanadium (V) with the plutonium determination and of bismuth (III) and copper (II) with the uranium determination can be corrected for if the exact amounts of these elements in the sample are known. The elements are reduced quantitatively under the conditions of the determination.
- 1.4.8.3. If the sample contains plutonium in other valency states than 4 it must be treated with hydroxylamine hydrogensulphate and sodium nitrite as described in procedure 2.2. section 2.2.6.2.



## 1.5. Standardization of cerium (IV) sulphate solution

### 1.5.1. Scope

The method is applicable to the standardization of 0.1 or 0.01 N cerium (IV) sulphate solution.

### 1.5.2. Principle

A known amount of arsenic (III) oxide is dissolved and titrated with the cerium (IV) sulphate solution to be standardized, using iron (II) 1,10-phenanthroline as an indicator. Osmium (VIII) oxide is used to catalyse the oxidation of arsenic (III) by cerium (IV).

### 1.5.3. Apparatus

- a) 1 400-ml beaker
- b) 1 50-ml measuring cylinder
- c) 1 10-ml pipette
- d) 1 100-ml volumetric flask
- e) 1 25-ml measuring cylinder
- f) 1 250-ml conical flask
- g) 1 50-ml burette
- h) 1 1000-ml volumetric flask
- i) 1 1-ml measuring pipette

### 1.5.4. Reagents

a) Cerium (IV) sulphate solution, 0.1 or 0.01 (t) N :  
add 27 ml of concentrated sulphuric acid in the case of 0.1 N solution or 270 ml in the case of 0.01 N solution to 40.4 g of cerium (IV) sulphate tetrahydrate. Add carefully water and dissolve the salt. Dilute with water to 1 l (0.1 N solution) or 10 l (0.01 N solution).

b) Iron (II) 1,10-phenanthroline indicator : dissolve 294 mg of iron (II) ammonium sulphate hexahydrate  $(\text{NH}_4)_2 \text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  in water and dilute to about 80 ml. Next, dissolve in this solution 594 mg of 1,10-phenanthroline monohydrate ( $\text{C}_{12} \text{H}_8 \text{N}_2 \cdot \text{H}_2\text{O}$ ) or 650 mg of 1,10-phenanthroline hydrochloride. Make up with water to 300 ml.

c) Arsenic (III) oxide, previously dried at  $110^\circ\text{C}$  and stocked over pure concentrated sulphuric acid.

d) Sulphuric acid, 3.7 M: add 25 ml of concentrated sulphuric acid to 100 ml of water and cool.

e) Sodium hydroxide solution, 1 M: dissolve 40 g of sodium hydroxide in water and dilute with water to 1 l.

f) Osmium (VIII) oxide solution, 0.04 M: dissolve 100 mg of osmium (VIII) oxide in 10 ml of 1 M sodium hydroxide solution. Store in the darkness. The solution can be kept unchanged for 1-2 months.

#### 1.5.5. Procedure

Weigh out to the nearest 0.1 mg 1000 (p) mg of arsenic (III) oxide and transfer with as little water as possible to a 400-ml beaker. Add 50 ml of 1 M sodium hydroxide solution, swirl and heat - if necessary - until the arsenic (III) oxide has completely dissolved.

In the case of the standardization of 0.01 N Cerium (IV) sulphate solution, transfer to a 1000-ml volumetric flask and make up to volume with water (solution A). In the case of the standardization of 0.1 N cerium (IV) sulphate solution, transfer to a 100 ml volumetric flask and make up to volume with water (solution B). Add 25 ml of sulphuric acid to 10 ml of either solution A or solution B, previously pipetted into a 250 ml conical flask. Dilute with water to 100 ml, add 5 drops of osmium (VIII) oxide solution and 0.5 ml of iron (II)

1.10-phenanthroline solution. Titrate with 0.1 or 0.01 (t) N cerium (IV) sulphate solution until the colour disappears ( $v_1$  ml consumed). In the same way carry out a blank taking 50 ml of sodium hydroxide solution instead of the arsenic solution ( $v_2$  ml consumed).

#### 1.5.6. Calculation

The exact titre of the solution is:

$$\text{for } 0.1 \text{ N} \quad t = \frac{p}{494.6 (v_1 - v_2)}$$

$$\text{for } 0.01 \text{ N} \quad t = \frac{p}{4946 (v_1 - v_2)}$$

Report the result to the nearest 0.0001 for 0.1 N solutions and to the nearest 0.00001 for 0.01 N solutions.

2. THE DETERMINATION OF PLUTONIUM AND URANIUM IN FUELS AND THEIR COMPONENTS. PROCEDURES FOR DISSOLUTION AND FUSION OF SAMPLES

2.1. Determination of plutonium and/or uranium in plutonium metal, uranium metal, plutonium-uranium alloys, plutonium nitride, plutonium-uranium nitrides and plutonium-uranium oxides

2.1.1. Scope

The method is applicable to the determination of from 0.005 % to 100 % plutonium and/or of from 4 % to 100 % uranium in plutonium metal, uranium metal, plutonium-uranium alloys, plutonium nitride and plutonium-uranium nitrides and of from 0.005 % to 1 % plutonium and/or of from 4 % to 100 % uranium in plutonium-uranium oxides.

2.1.2. Principle

The sample is dissolved in a mixture of nitric acid and hydrofluoric acid. After dilution plutonium and/or uranium are determined according to procedures 1.1.or 1.2 and/or 1.3. respectively.

2.1.3. Apparatus

- a) 1 100-ml round bottom flask connected with a refrigerating column
- b) 1 50-ml volumetric flask
- c) 1 50-ml measuring cylinder

2.1.4. Reagents

a) nitric acid-hydrofluoric acid mixture: dilute 146 ml of 14 M nitric acid with water to 200 ml and add 0.39 g of ammonium fluoride. Dissolve and mix.

2.1.5. Sample

From the metal or the alloy prepare about 2 g of shavings. Carry out this operation in an inert gas atmosphere. Grind pellets and coarse powders in a mortar. Carry out this operation in an inert gas atmosphere in the case of nitrides.

2.1.6. Procedure

Place 30 ml of nitric acid-hydrofluoric acid mixture in the round bottom flask. Weigh out to the nearest 0.1 mg 500 (p) mg of sample in an inert gas atmosphere, when the sample consists of metal, alloy or nitride, and add these carefully to the acid mixture. Place the refrigerating column on the round bottom flask and heat until a clear solution is obtained. Cool, transfer to a 50-ml volumetric flask and make up to volume with water. In suitable aliquots of this solution ( $v_1$  and  $v_2$  ml respectively) determine plutonium according to procedure 1.1. when the content is over 1% or according to procedure 1.2. for lower contents and/or determine uranium according to procedure 1.3. (A or A' mg of plutonium and/or B mg of uranium found).

2.1.7. Calculation

The sample contains :

$$\frac{A \cdot 10^4}{2 v_1 p} \% \quad \text{or} \quad \frac{A' \cdot 10^4}{2 v_1 p} \% \quad \text{plutonium}$$

$$\frac{B \cdot 10^4}{2 v_2 p} \% \quad \text{uranium}$$

Report the results to the nearest 0.02 % (procedure 1.1.), 0.005 % (procedure 1.2.) and 0.05 % (procedure 1.3.).



2.2. Determination of plutonium and/or uranium in plutonium oxide and plutonium-uranium oxides

2.2.1. Scope

The method is applicable to the determination of from 1 to 100% plutonium and/or of from 2 to 100 % uranium in plutonium oxide and plutonium-uranium oxides respectively.

2.2.2. Principle

The sample is dissolved either by fusion with a mixture of sodium pyrosulphate and potassium pyrosulphate, followed by dissolution of the melt in nitric acid, or by boiling with sulphuric acid, nitric acid and ammonium sulphate. In the first case plutonium and uranium are determined according to procedures 1.1 and 1.3 respectively, whereas in the second case these elements are determined according to procedure 1.4.

2.2.3. Apparatus

2.2.3.1. Fusion procedure

- a) 1 50-ml quartz beaker
- b) 1 watch glass
- c) 1 25-ml measuring cylinder
- d) 1 50-ml volumetric flask
- e) 1 electric burner.

2.2.3.2. Dissolution procedure

- a) 1 100-ml round bottom flask provided with a refrigerating column
- b) 1 10-ml measuring cylinder
- c) 1 1-ml measuring pipette
- d) 1 25-ml measuring cylinder
- e) 1 50-ml volumetric flask

## 2.2.4. Reagents

### 2.2.4.1. Fusion procedure

- a) Pyrosulphate mixture : mix 60 g of sodium pyrosulphate with 15 g of potassium pyrosulphate.
- b) Nitric acid, 5 M : dilute 100 ml of concentrated nitric acid with water to 280 ml.

### 2.2.4.2. Dissolution procedure

- a) Sulphuric acid, about 9 M : add carefully 100 ml of concentrated sulphuric acid to 100 ml of water, mix and cool.
- b) Nitric acid, 14 M.
- c) Ammonium sulphate, solid.
- d) Hydroxylamine hydrogensulphate, solid.
- e) Sodium nitrite, solid.

## 2.2.5. Sample

The sample should consist of a fine powder. If otherwise, grind coarse powders or pellets in a mortar.

## 2.2.6. Procedure

### 2.2.6.1. Fusion procedure

Weigh out to the nearest 0.1 mg 500 (p) mg of sample and transfer to a 50-ml quartz beaker. Add 5 g of the pyrosulphate mixture and mix thoroughly. Cover the beaker with a watch glass and heat carefully on an electric burner to about 400°C until a clear melt is obtained. Cool, dissolve in 15 ml of 5 M nitric acid, transfer to a 50 ml volumetric flask and make up to volume with water. In suitable aliquots of this solution ( $v_1$  and  $v_2$  ml respectively) determine plutonium and/or uranium according to procedures 1.4 and/or 1.3 respectively (A mg of plutonium and/or B mg of uranium found).

### 2.2.6.2. Dissolution procedure

Weigh out to the nearest 0.1 mg 500 (p) mg of sample and transfer to a 100-ml round bottom flask. Add 5 ml of 9 M sulphuric

acid, 1 ml of 14 M nitric acid and 2.5 g of ammonium sulphate. Place the refrigerating column on the round bottom flask, heat to boiling and boil under reflux for 10 min. Take off the refrigerating column, heat to boiling for 30 min. in order to eliminate nitrate and to complete dissolution, and cool. Carefully add 20 ml of water, cool and add hydroxylamine hydrogensulphate until the colour changes to bluish green. Heat to about 80°C for 5 min., cool, add 200 mg of sodium nitrite and heat to expel nitrous oxide vapours. Cool, transfer to a 50-ml volumetric flask and make up to volume with water. Determine plutonium and uranium in  $v_3$  ml (maximum 10 ml) of this solution according procedure 1.4 (A'' mg of plutonium and B' mg of uranium found).

#### 2.2.7. Calculation

The sample contains

$$\frac{A \cdot 10^4}{2 v_1 p} \% \quad \text{or} \quad \frac{A'' \cdot 10^4}{2 v_3 p} \% \quad \text{plutonium}$$

$$\frac{B \cdot 10^4}{2 v_2 p} \% \quad \text{or} \quad \frac{B' \cdot 10^4}{2 v_3 p} \% \quad \text{uranium}$$

Report the results to the nearest 0.02 % for plutonium and to the nearest 0.05 % for uranium.

2.3. Determination of plutonium and/or uranium in plutonium carbide, uranium carbide and plutonium-uranium carbides

2.3.1. Scope

The method is applicable to the determination of from 1 to 100 % plutonium and/or of from 2 to 100 % uranium in plutonium carbide, uranium carbide and plutonium-uranium carbides (see 2.3.8.).

2.3.2. Principle

The sample is calcined to obtain the corresponding oxides which are subsequently either fused with a mixture of sodium pyrosulphate and potassium pyrosulphate and dissolved in nitric acid, or dissolved directly by boiling with sulphuric acid, nitric acid and ammonium sulphate. In the first case plutonium and/or uranium are determined according to procedures 1.1 and 1.3 respectively whereas in the second case these elements are determined according to procedure 1.4.

2.3.3. Apparatus

2.3.3.1. Fusion procedure

- a) 1 furnace capable of heating up to 1000°C
- b) 1 electric burner
- c) 1 50-ml quartz beaker
- d) 1 watch glass
- e) 1 25-ml measuring cylinder
- f) 1 50-ml volumetric flask

### 2.3.3.2. Dissolution procedure

- a) 1 furnace capable of heating up to 1000°C
- b) 1 100-ml quartz round bottom flask provided with a refrigerating column
- c) 1 10-ml measuring cylinder
- d) 1 1-ml measuring pipette
- e) 1 25-ml measuring cylinder
- f) 1 50-ml volumetric flask

### 2.3.4. Reagents

#### 2.3.4.1. Fusion procedure

- a) Pyrosulphate mixture: mix 60 g of sodium pyrosulphate with 15 g of potassium pyrosulphate.
- b) Nitric acid, 5 M: dilute 100 ml of concentrated nitric acid with water to 280 ml.
- c) Oxygen

#### 2.3.4.2. Dissolution procedure

- a) Sulphuric acid, about 9 M : add carefully 100 ml of concentrated sulphuric acid to 100 ml of water, mix and cool.
- b) Nitric acid, 14 M
- c) Ammonium sulphate, solid
- d) Oxygen
- e) Hydroxylamine hydrogensulphate, solid
- f) Sodium nitrite, solid

### 2.3.5. Sample

The sample should consist of a fine powder. In the case of pellets and coarse powders grind them in a mortar in an inert gas atmosphere.



### 2.3.6. Procedure

#### 2.3.6.1. Fusion procedure

Weigh out to the nearest 0.1 mg 500 (p) mg of sample, transfer to a 50-ml quartz beaker and place this into the furnace. Heat to about 800°C in a stream of oxygen for 30 min., cool, take the beaker out of the furnace, add 5 g of the pyrosulphate mixture and mix thoroughly. Cover the beaker with a watch glass and heat carefully on an electric burner to about 400°C until a clear melt is obtained. Cool, dissolve in 15 ml of 5 M nitric acid, transfer to a 50-ml volumetric flask and make up to volume with water. In suitable aliquots of this solution ( $v_1$  and  $v_2$  ml respectively) determine plutonium and/or uranium according to procedures 1.1 and/or 1.3 respectively. (A mg of plutonium and/or B mg of uranium found).

#### 2.3.6.2. Dissolution procedure

Weigh out to the nearest 0.1 mg 500 (p) mg of sample, transfer to a 100-ml quartz round bottom flask and place this in the furnace. Heat to about 800°C in a stream of oxygen for 30 min., cool, take the flask out of the furnace, and add 5 ml of 9 M sulphuric acid, 1 ml of 14 M nitric acid and 2.5 g of ammonium sulphate. Place the refrigerating column on the round bottom flask, heat to boiling and boil under reflux for 10 min. Take off the refrigerating column, heat to boiling for 30 min. in order to eliminate nitrate and to complete dissolution, and cool. Carefully add 20 ml of water, cool and add hydroxylamine hydrogensulphate until the colour changes to bluish green. Heat to about 60°C for 5 min., cool, add 200 mg of sodium nitrite and heat to expel nitrous oxide vapours. Cool, transfer to a 50 ml volumetric flask and make up to volume with water. Determine plutonium and uranium in  $v_3$  ml (at maximum 10 ml) of this solution according to procedure 1.4. (A'' mg of plutonium and B' mg of uranium found).

2.3.7. Calculation

The sample contains :

$$\frac{A \cdot 10^4}{2 v_{1p}} \% \quad \text{or} \quad \frac{A'' \cdot 10^4}{2 v_{3p}} \% \quad \text{plutonium}$$

$$\frac{B \cdot 10^4}{2 v_{2p}} \% \quad \text{or} \quad \frac{B' \cdot 10^4}{2 v_{3p}} \% \quad \text{uranium.}$$

Report the results to the nearest 0.02 % for plutonium and to the nearest 0.05 % for uranium.

2.3.8. Remarks

2.3.8.1. In the case of plutonium-uranium carbides containing of from 0.05 to 1 % of plutonium, this element can be determined by calcination in oxygen, dissolution in nitric acid - hydrofluoric acid as described in procedure 2.1. and application of procedure 1.2 (spectrophotometric determination of plutonium).

2.3.8.2. In the case of pure uranium carbide the fusion step can be omitted. After calcination the oxide is dissolved directly in nitric acid according to procedure 2.4.

## 2.4. Determination of uranium in uranium nitride and uranium oxide

### 2.4.1. Scope

The method is applicable to the determination of uranium in uranium nitride and uranium oxide.

### 2.4.2. Principle

The sample is dissolved in nitric acid and uranium is determined according to procedure 1.3.

### 2.4.3. Apparatus

- a) 1 100-ml round bottom flask provided with a refrigerating column
- b) 1 50-ml measuring cylinder
- c) 1 50-ml volumetric flask

### 2.4.4. Reagents

Nitric acid, 7 M : dilute 100 ml of concentrated nitric acid with water to 200 ml.

### 2.4.5. Sample

The sample should be a powder. Grind pellets in a mortar. In the case of nitride samples carry out this operation in an inert gas atmosphere.

### 2.4.6. Procedure

Weigh out to the nearest 0.1 mg 500 (p) mg of sample and transfer to a 100-ml round bottom flask. Add 30 ml of 7 M nitric acid, place the refrigerating column on the round bottom flask and heat to boiling until a clear solution is obtained. Cool, transfer to a 50-ml volumetric flask and make up to volume with water. In 10 ml of this solution determine uranium according to procedure 1.3 (B mg of uranium found).

2.4.7. Calculation

The sample contains

$$\frac{B \cdot 10^3}{2 p} \% \text{ uranium}$$

Report the results to the nearest 0.05 %.

### 3. PROCEDURES FOR THE DIRECT ANALYSIS OF FUELS AND THEIR COMPONENTS

#### 3.1. Determination of carbon in plutonium metal, uranium metal, plutonium-uranium alloys, plutonium oxide, uranium oxide, plutonium-uranium oxides, plutonium carbide, uranium carbide, plutonium-uranium carbides, plutonium nitride, uranium nitride, plutonium uranium nitrides

##### 3.1.1. Scope

The method is applicable to the determination of from 20 to 4000  $\mu\text{g}$  of carbon in the elements and compounds mentioned in the title.

##### 3.1.2. Principle

The sample is heated in air and oxygen and the carbon contained in it is oxidized to carbon dioxide which is evolved and subsequently absorbed in a solution of sodium hydroxide. The conductivity of this solution is measured before and after the absorption of carbon dioxide. The carbon content is determined from the difference between the results of the two measurements.

##### 3.1.3. Apparatus

- a) 1 high-frequency furnace, 0.5 kW
- b) 2 crucibles of ceramic material, previously heated at  $1000^{\circ}\text{C}$  for 8 hours
- c) 1 gas absorption apparatus with inserted platinum electrodes which are connected to the wheatstone bridge (see 3.1.9.1.).
- d) 1 wheatstone bridge with automatic correction for temperature changes of the solution to be analysed and modified in such a way that the compensating variable resistance is linearly proportional to the concentration of sodium hydroxide solution in the absorption apparatus (see 3.1.9.1.)
- e) 1 membrane pump with rotameter, capacity 90 ml/min.

#### 3.1.4. Reagents

- a) Sodium hydroxide solution, 0.05 N : dissolve 2 g of sodium hydroxide in water and dilute to 1-l.
- b) Copper disks with a diameter which is slightly smaller than that of the crucible mentioned under 3.1.3.b and **weighing** about 0.75 g
- c) Carbon dioxide-free oxygen.
- d) Carbon dioxide-free air.
- e) Standard steel samples with certified carbon content (see 3.1.9.2.)
- f) Carbon tetrachloride.

#### 3.1.5. Sample

- 3.1.5.1. Metals and alloys: in an inert gas atmosphere prepare about 3 g of shavings. Degrease them by washing with carbon tetrachloride.
- 3.1.5.2. Oxides, carbides and nitrides : grind 3 g of pellets in a carbon-free mortar. Carry out this operation in an inert gas atmosphere in the case of nitrides and carbides. Powders do not need any preparation.

#### 3.1.6. Procedure

Weigh out to the nearest mg 1000 (p) mg of sample in the case of determination of traces of carbon or weigh out to the nearest 0.01 mg 50 (p) mg of sample in the case of the analysis of carbides. **Transfer it to the crucible on the bottom of which** has been put a copper disk. Cover the sample with another copper disk and transfer the crucible to the induction furnace. Connect the furnace on one side with a source of carbon dioxide-free oxygen (in the case of oxide, carbides and nitrides) or a source of carbon dioxide-free air (in the case of metals and alloys) and on the other side with the gas absorption apparatus. Introduce so much sodium hydroxide solution into the absorption apparatus that all electrodes are inserted in the solution (see 3.1.9.3.). Measure the conductivity of the sodium hydroxide solution ( $r_0$  found). Pass

a stream of air (in the case of metals and alloys) through the whole system and heat up to 600°C for 1 min. Shut off the stream of air and pass oxygen through the system at a rate of about 90 ml per min. and heat at maximum capacity until the anode current has decreased to the value which is reached when the furnace is switched on under unloaded conditions. (see 3.1.9.4.). Switch off the furnace. In the case of oxides, carbides and nitrides pass a stream of oxygen **through the system** at a rate of 90 ml per min. and heat at maximum capacity until the anode current has decreased to the value which is reached when the furnace is switched on under unloaded conditions (see 3.1.9.4.). Switch off the furnace. In both cases wait 10 min. Measure the conductivity of the sodium hydroxide solution ( $r_2$  found), disconnect the absorption apparatus from the system and interrupt the stream of oxygen. Carry out a blank by applying the procedure to a crucible which contains only two copper disks ( $r_1'$  and  $r_2'$  respectively are found). From the corrected conductivity  $\left[ (r_1 - r_2) - (r_1' + r_2') \right]$  determine the amount of carbon with the aid of a calibration graph (a  $\mu\text{g}$  found).

### 3.1.7. Calculation

The sample contains :

$$\frac{1000 a}{p} \text{ ppm of carbon or } \frac{a}{10p} \% \text{ carbon}$$

Report the results to the nearest 2 ppm in the case of traces and to the nearest 0.01 % in the case of carbides.

### 3.1.8. Calibration graph

Carry standard steel samples with certified carbon contents through the procedure, omitting the use of copper disks and, consequently, the blank. Plot the measured decreases of the conductivity of the sodium hydroxide solutions against the corresponding amounts of carbon in  $\mu\text{g}$ , taken into operation.

3.1.9. Remarks

- 3.1.9.1. Instead of the absorption and measuring apparatus described above other apparatus especially constructed for the purpose can be used, e.g. the apparatus of Messrs Wösthoff, Bochum, Germany.
- 3.1.9.2. Standard steel samples with certified carbon content may be obtained, e.g. from Bundesanstalt für Materialprüfung, Berlin-Dahlem, Germany.
- 3.1.9.3. The volume of sodium hydroxide solution used in these determinations must always be constant.
- 3.1.9.4. It is advisable to use a membrane pump with rotameter to maintain a continuous stream of oxygen, even after having switched off the furnace, so as to avoid that sodium hydroxide solution enters into the system.
- 3.1.9.5. It is advisable to check the procedure at regular intervals by carrying a standard steel sample through the procedure.



3.2. Gravimetric determination of the oxygen to metal ratio in plutonium oxide, uranium oxide and plutonium-uranium oxides

3.2.1. Scope

The method is applicable to the determination of the oxygen to metal ratio of plutonium oxides in the range of 1.5 to 2.0, of uranium oxides in the range of 2 to 2.67 and of plutonium-uranium oxides containing less than 30 % of plutonium oxide in the range of 1.85 to 2.27. Other elements may be present only in trace amounts.

3.2.2. Principle

The weighed sample is oxidized in air at 850 - 900°C (plutonium oxide) or equilibrated with a mixture of carbon monoxide and carbon dioxide at 850°-900°C (uranium oxide and plutonium-uranium oxides) and then reweighed. The oxygen to metal ratio is calculated from the difference between the two weighings.

3.2.3. Apparatus

- a) Platinum boats
- b) Microbalance which can be read to the nearest 0.001 mg (see 3.2.8).
- c) Furnace capable of heating up to 1000°C.

3.2.4. Reagents

- a) Mixture of carbon monoxide and carbon dioxide (10 + 1), free of metal carbonyls.
- b) Argon, free of oxidizing and reducing impurities and water.

3.2.5. Sample

Any pellet or powder.

3.2.6. Procedure

Carry out all manipulations in a perfectly dry inert atmosphere.

Weigh a platinum boat to the nearest 0.001 mg (t g). Weigh a piece of platinum which serves as a reference weight ( $r_1$  g). Choose the size of this piece of platinum such that its weight is comparable to that of the sample boat. Bring 200 to 500 mg of sample into the platinum boat and reweigh (p g). Transfer the boat with sample to the center of the heating tube in the furnace. Pass a stream of air - in the case of plutonium oxides - or carbon monoxide/carbon dioxide mixture - in the case of uranium oxides and mixed plutonium-uranium oxides - through the tube at a rate of 30 ml per h. Heat to 850 - 900°C and keep at this temperature overnight. Replace the carbon monoxide/carbon dioxide stream by an argon stream, cool to room temperature and weigh (q g). Weigh the reference weight ( $r_2$  g).

3.2.7. Calculation

Calculate the oxygen to metal ratio, O/M, according to

$$O/M = 2 - \frac{M}{16} \left[ \frac{(p-r_1)-(q-r_2)-w(p-t)10^{-6}}{(t-r_1)-(q-r_2)} \right]$$

where M = molecular weight of the sample after equilibration

p = weight of the **platinum** boat with sample before equilibration

q = weight of the **platinum** boat with sample after equilibration

t = weight of the empty platinum boat

$r_1$  = reference weight before equilibration

$r_2$  = reference weight after equilibration

w = water content in ppm, determined according to procedure 3.4.

Report the results to the nearest 0.0005.

3.2.8. Remarks

3.2.8.1. The determination can also be carried out using a macrobalance which can be read to the nearest 0.1 mg. The use of the reference weights can then be omitted. The results obtained are somewhat less precise than those obtained with the microbalance. Results should then be reported to the nearest 0.002.

3.2.8.2. The correction for the water content, as indicated in the formula in section 3.2.7. can be omitted when this content is lower than 60 ppm.

### 3.3. Coulometric determination of the oxygen to metal ratio in uranium oxide

#### 3.3.1. Scope

The method is applicable to the determination of the oxygen to metal ratio in uranium oxide. Traces of impurities normally present do not interfere.

#### 3.3.2. Principle

The sample is dissolved in concentrated phosphoric acid and uranium (VI) is reduced at the mercury electrode at  $-0.35$  V vs silver - silver chloride electrode. Uranium (IV) is oxidized to uranium (VI) with potassium dichromate and excess dichromate is reduced at  $+0.1$  V. Total uranium is subsequently reduced at  $-0.35$  V. The oxygen to metal ratio is calculated from the results of the two uranium reductions.

#### 3.3.3. Apparatus

- a) 1 controlled potential coulometer with electronic potentiostat and electronic integrator, provided with a digital voltmeter.
- b) 1 electrolysis cell with a mercury pool electrode, platinum wire helix and silver-silver chloride electrode according to fig. 3 (see procedure 1.4).
- c) 1 100-ml volumetric flask
- d) 1 25-ml measuring cylinder
- e) 1 5-ml measuring cylinder
- f) 1 5-ml pipette
- g) 1 5-ml measuring pipette
- h) 1 100-ml conical flask.

3.3.4. Reagents

- a) Mercury, distilled twice
- b) Phosphoric acid, 85 %: pass a stream of oxygen-free nitrogen through the acid for 4 h and stock in an inert gas atmosphere.
- c) Sulphuric acid, 1 M : add 56 ml of concentrated sulphuric acid to 500 ml of water, cool and dilute to 1 l. Pass a stream of oxygen-free nitrogen through the acid for 30 min. and stock in an inert gas atmosphere.
- d) Potassium dichromate solution, 0.016 M : weigh out 5 g of potassium dichromate, dissolve in water and make up to 1 l.
- e) Nitrogen, oxygen free.

3.3.5. Sample

Crush the sample in a mortar in an inert gas atmosphere.

3.3.6. Procedure

Weight out 500 mg of sample and transfer to a 100-ml conical flask. Pass a stream of nitrogen over the sample and after 20 min. add 20 ml of 85 % phosphoric acid. Heat until a clear solution is obtained, cool, interrupt the stream of nitrogen and transfer to a 100-ml volumetric flask. Rinse the conical flask with 1 M sulphuric acid and add this to the phosphoric acid solution. Make up to volume with 1 M sulphuric acid and stock in an inert gas atmosphere. Transfer to the electrolysis cell 5 ml of mercury and 5 ml of 1 M sulphuric acid. Pass a strong stream of nitrogen through the solution. After 5 min. pass it over the solution. Pipette 5 ml of the uranium solution into the cell. Reduce the dissolved mercury at +0.1 V vs silver-silver chloride electrode until the current has decreased to 20  $\mu$ A. Set the potential at zero, switch on the electrolysis current and lower slowly the potential to -0.35 V. Reduce until the current has decreased to 20  $\mu$ A

and measure the quantity of electricity in coulomb which has flown since the potential was set at  $-0.35$  V ( $Q_1$ ). The residual current be  $i_1$  Amps and the electrolysis time be  $t_1$  sec. Set the potential at  $+0.1$  V and add dropwise potassium dichromate solution until a strong increase of the current indicates the presence of excess dichromate. Reduce the excess dichromate until the current has decreased to  $20$   $\mu$ A. Put the integrator at zero. Lower slowly the potential to  $-0.35$  V and reduce until the current has become  $20$   $\mu$ A. Interrupt the stream of nitrogen, measure the quantity of electricity flown ( $Q_2$ ), the residual current ( $i_2$  Amps) and the electrolysis time ( $t_2$  sec).

### 3.3.7. Calculation

The oxygen to metal ratio, O/M, is

$$O/M = 2.0000 + \frac{Q_1}{Q_2}$$

In the case of oxygen to metal ratios of nearly 2.00 correct for the residual currents and calculate O/M according to

$$O/M = 2.000 + \frac{Q_1 - i_1 t_1}{Q_2 - i_2 t_2}$$

Report the results to the nearest 0.0002 for  $2 < O/M < 2.1$  and to the nearest 0.001 for  $O/M > 2.1$ .

3.4. Coulometric determination of traces of water in plutonium oxide, uranium oxide and plutonium-uranium oxides

3.4.1. Scope

The method is applicable to the determination of from 10 to 10,000  $\mu\text{g}$  of water in plutonium oxide, and mixed plutonium-uranium oxides.

3.4.2. Principle

The sample is heated at  $700^{\circ}\text{C}$  under nitrogen and the water vapour evolved is absorbed on a phosphorus (V) oxide layer in a Keidel cell. The acid formed is decomposed electrolytically on platinum electrodes. The quantity of water is then determined from the quantity of current consumed in the electrolysis.

3.4.3. Apparatus

a) Moisture analyzer 26321 AMA, Consolidated Electrodynamics Corporation.

3.4.4. Reagents

- a) Nitrogen, dry.
- b) Copper (II) sulphate pentahydrate, solid.

3.4.5. Sample

Any pellet or powder.

3.4.6. Procedure

Pass a stream of nitrogen through the apparatus at a rate of 90 ml per min. Rinse the apparatus with the carrier gas for 10 min. Switch on the electrolysis cell and perform the electrolysis until a constant blank is obtained. This takes about 30 min. Weigh out 2 to 20 (p) g of sample to the nearest mg and transfer it to the furnace. Heat to 700°C and carry out the electrolysis until a constant blank is obtained. The blank be a  $\mu\text{g}$  of water per min. Cool and take the sample out of the furnace. The total quantity of water read on the integrator be b  $\mu\text{g}$  and the time of analysis be t min.

3.4.7. Calculation

The sample contains :

$$w = \frac{(b-at)C}{p} \text{ ppm of water}$$

where a = quantity of water in the blank in  $\mu\text{g}$  per min

b = total quantity of water in  $\mu\text{g}$  measured

t = time of the determination

C = correction factor (see 3.4.3.)

p = weight of sample in g.

Report the results to the nearest 1/p ppm.

3.4.8. Calibration

Weigh out to the nearest 0.1 mg 10 portions of about 5 mg each of sieved copper (II) sulphate pentahydrate with particle size between 0.5 and 1 mm, and carry these portions through the entire procedure.

Determine the average water content (A %). Also determine the water content by drying at 300°C until constant weight (B %). The correction factor C is A/B.



3.5. Emission spectrographic determination of traces of metals in plutonium metal, uranium metal, plutonium-uranium alloys plutonium nitride, uranium nitride, plutonium-uranium nitrides, plutonium carbide, uranium carbide, plutonium-uranium carbides, plutonium oxide, uranium oxide and plutonium-uranium oxides.

3.5.1. Scope

The method is applicable to the determination of the amounts of the elements, indicated in table 3, in plutonium oxide, triuranium octoxide and a mixture of plutonium oxide and triuranium octoxide containing 10 to 20 % plutonium oxide, which may be obtained from the respective metals, alloys, nitrides, carbides and oxides (see 3.5.9.1.).

Table 3

Element to be determined	Scope		
	plutonium oxide	triuranium octoxide	plutonium oxide + tri-uranium octoxide (15+85)
Silicon	10-400 ppm	30 - 300 ppm	30 - 300 ppm
Phosphorus	-	15 - 500	40 - 400
Aluminium	50-500	15 - 500	30 - 500
Iron	15 - 500	15 - 500	15 - 500
Magnesium	3 - 100	5 - 100	2 - 100
Manganese	2 - 50	1 - 50	2 - 50
Lead	2 - 50	1 - 50	1 - 50
Chromium	4 - 100	10 - 100	5 - 100
Tin	2 - 50	1 - 50	1 - 50
Nickel	4 - 100	5 - 100	4 - 100
Bismuth	5 - 50	1 - 50	1 - 50
Molybdenum	-	5 - 50	15 - 60
Calcium	-	100 - 500	-
Vanadium	-	40 - 100	15 - 100
Copper	2 - 50	5 - 50	5 - 50
Silver	-	0,2 - 50	0,2- 4
Sodium	-	40 - 400	40 - 300
Zinc	30 - 500	50 - 500	50 - 500

Principle

The sample is dissolved, the solution obtained is evaporated to dryness and the residue is calcined. After addition of gallium oxide and traces of cobalt oxide - which serves as an internal standard - the mixture is placed in a graphite electrode which is subsequently excited at a DC arc. The emission spectrum is taken and the quantities of elements are determined with the aid of calibrating graphs.

3.5.3. Apparatus

- a) Spectrograph; **grating 15,000 grooves/inch, linear dispersion 2.5 Å/mm in the second order.**
- b) Generator 0 - 20 Amps
- c) Comparator microphotometer
- d) Spectroprojector, magnification 20 x
- e) Photographic emulsion KODAK SA 1
- f) 1 furnace capable of heating up to 1000°C
- g) 1 tungsten carbide mortar
- h) 1 mechanical mixer
- i) 1 platinum crucible, height 50 mm, diameter 30 mm
- j) 1 10-ml measuring cylinder
- k) 1 electric burner
- l) graphite anodes, height 15.9 mm with two cylindrical holes viz. one with depth 3.97 mm and diameter 3.18 mm allowing the electrode to be placed on a support, and one with depth 7.19 mm and diameter 4.75 mm which contains the sample.
- m) graphite cathodes, height 33.1 mm and diameter 3.05 mm
- n) 1 apparatus for the electrode preparation according to figs. 4 and 5.
- o) 1 100-ml round bottom flask provided with a refrigerating column (only for analysis of plutonium oxide and plutonium-uranium oxides.).

#### 3.5.4. Reagents

- a) Gallium oxide - cobalt oxide mixture: weigh out 10 g of gallium oxide, add 5 mg of cobalt oxide and mix well.
- b) Nitric acid, 14 M (for the analysis of metal, alloys, nitrides, carbides and uranium oxide).
- c) Sulphuric acid, 9 M : add carefully 100 ml of concentrated sulphuric acid to 100 ml of water, mix and cool (for the analysis of plutonium oxide and plutonium-uranium oxides).
- d) Ammonium sulphate, solid (for the analysis of plutonium oxide and plutonium-uranium oxides).
- e) Formic acid, 98 % (for the analysis of metals, alloys, nitrides, carbides and uranium oxide).
- f) Acetic acid, 5 % : Weigh out 50 g of glacial acetic acid and dilute with water to 1 l.
- g) KODAK T 19.
- h) KODAK special.
- i) Standard triuranium octoxide samples. N.B.S 95 - 1/7.
- j) Standard plutonium oxide samples (see 3.5.9.2).

#### 3.5.5. Sample

From the metal and the alloys prepare about 2 g of shavings. Grind pellets in a mortar until a powder is obtained. For this purpose use a tungsten carbide mortar (see 3.5.9.3.). Carry out these operations in an inert gas atmosphere in the case of metals, alloys, nitrides or carbides.

#### 3.5.6. Procedure

##### 3.5.6.1. Sample preparation of metals, alloys, nitrides, carbides and uranium oxide

Weigh out 1 to 1.5 g of sample and transfer to a platinum crucible. Carry out this operation in an inert gas atmosphere, when the sample consists of metals, alloys, nitrides or carbides. Add carefully 10 ml of 14 M nitric acid and heat until a clear solution is obtained. Evaporate to dryness, add 4 ml of 98% formic acid, heat, evaporate to dryness, heat at 900°C for 1 h and cool. Preserve the residue for further treatment according to section 3.5.6.3.

### 3.5.6.2. Sample preparation of plutonium oxide and plutonium-uranium oxides

Weigh out 1 to 1.5 g of sample and transfer to a 100-ml round bottom flask. Add 10 ml of 9 M sulphuric acid and 5 g of ammonium sulphate and heat to fuming. Continue heating to boiling for 30 min. Cool, and add carefully 5 ml of water. If a residu is observed, heat to eliminate the water and from that moment on heat to boiling for 30 min. Cool and transfer the clear solution to a platinum crucible, evaporate to dryness, heat to 700°C for 30 min. and then heat to 900°C for 1 h and cool.

### 3.5.6.3. Electrode preparation

Weigh out 980 mg of the oxides obtained according to sections 3.5.6.1 or 3.5.6.2., add 20 mg of gallium oxide-cobalt oxide mixture, mix well and homogenize using a mechanical mixer for 3 min. Transfer 100 mg of the mixture to the graphite anode and place it into the holder A of the apparatus for the electrode preparation (figs. 4 and 5). Turn the crank C and let the electrode fall freely five times. Next, introduce the vent-forming needle into the powder and turn the crank F so that the needle turns five times 180° back and forth. In this way prepare three electrodes and transfer them to the electrode stand.

### 3.5.6.4. Spectrographic analysis

Put the electrodes into the stand and take the spectra in the region 2400 - 3700 Å under the conditions given in table 4.

Table 4

	plutonium oxide	triuranium octoxide	plutonium oxide + tri- uranium octoxide (15 + 85)
DC arc starting	15 Amps	10 Amps	10 Amps
preburn period	5 sec	5 sec	5 sec
exposure time	40 sec	40 sec	40 sec
electrode gap	4 mm	4 mm	4 mm
	center in the optical path by projection	center in the optical path by projection	center in the op- tical path by projection
slit width	15 $\mu$	25 $\mu$	25 $\mu$
sector setting	100 % - 11,6% transmission	100 % - 10 % transmission	100 % - 10 % transmission

Take the plate out of the spectrograph and carry out the photographic processing as follows :

development : KODAK T 19 for 3 min. at  $20^{\circ}\text{C} \pm 0,5^{\circ}\text{C}$   
 stop bath : acetic acid, 5 % for 10 sec.  
 fixing : KODAK special for 3 min.  
 washing : running water for 30 min,  
 drying : air current at  $30^{\circ}\text{C}$  for 15 min.

Check the spectra with the aid of the spectroprojector and carry out the densitometric measurements using the lines indicated in tables 5, 6 and 7.

Table 5

Matrix : plutonium oxide

Reference line : cobalt 2521.36 Å

Element to be determined	sector setting	concentration range	analytical line
Silicon	11.6 %	10 - 400 ppm	2516.12 Å
Iron	11.6	15 - 500	2599.39
Magnesium	100	3 - 100	2779.83
Manganese	11.6	2 - 50	2801.06
Lead	11.6	2 - 50	2833.07
Chromium	100	4 - 100	2843.25
Tin	11.6	15 - 50	2863.33
	100	2 - 15	2863.33
Bismuth	100	5 - 50	2989.03
Nickel	100	4 - 100	3002.49
Aluminium	100	50 - 500	3092.71
Copper	11.6	2 - 50	3273.96
Zinc	100	30 - 500	3302.59

Table 6

Matrix: triuranium octoxide

Element to be determined	Sector setting	concentration range	analytical line	cobalt reference line
Silicon	10 %	30 - 300	2519.21	2521.36
Phosphorus	100	15 - 500	2553.28	id
Aluminium	100	15 - 500	2575.41	id
Iron	10	40 - 500	2599.40	id
	100	15 - 40	2599.40	id
Magnesium	100	5 - 100	2779.83	3044.01
Manganese	10	10 - 50	2801.06	id
	100	1 - 10	2801.06	id
Lead	10	20 - 50	2833.07	id
	100	1 - 20	2835.07	id
Chromium	100	10 - 100	2843.25	id
Tin	100	1 - 50	2863.33	id
Nickel	100	5 - 100	3002.49	id
Bismuth	100	1 - 50	3067.72	id
Molybdenum	100	5 - 50	3170.75	2521.36
Calcium	100	100 - 500	3179.33	id
Vanadium	100	40 - 100	3183.98	id
Copper	100	5 - 50	3247.54	id
Silver	100	0,2- 50	3280,68	id
Sodium	100	40 - 400	3302.29	id
Zinc	100	50 - 500	3302.59	id

Table 7

Matrix: plutonium oxide-triuranium octoxide mixture (15+85)

Element to be determined	Sector setting	Concentration range	Analytical line	Cobalt reference line
Silicon	10 %	30 - 300 ppm	2514.12 Å	2521.36 Å
Phosphorus	100	40 - 400	2553.28	id
Aluminium	100	30 - 500	2575.41	id
	100	15 - 100	3092.71	3044.01
Iron	10	30 - 500	2599.40	2521.36
Magnesium	100	10 - 100	2776.69	3044.01
	10	2 - 10	2802.69	id
Manganese	10	2 - 50	2801.06	id
Lead	10	10 - 50	2833.07	id
	100	1 - 10	2833.07	id
Chromium	10	25 - 100	2843.25	id
	100	5 - 50	2843.25	id
Tin	10	10 - 50	2863.33	id
	100	1 - 20	2863.33	id
Nickel	100	4 - 100	3002.49	id
Bismuth	10	10 - 50	3067.72	id
	100	1 - 20	3067.72	id
Molybdenum	100	15 - 60	3170.35	2521.36
Vanadium	100	15 - 100	3184.98	id
Copper	10	5 - 50	3247.54	id
Silver	100	0.2 - 4	3280.68	id
Sodium	100	40 - 300	3302.39	id
Zinc	100	50 - 500	3302.59	id



### 3.5.7. Calculation

From the results of the densitometric measurements calculate the quantities of the elements with the aid of calibration graphs for each of the three spectra taken. Calculate the average results and report them to the nearest 5 % of their value.

### 3.5.8. Calibration graphs

Prepare the calibration graphs by adding known amounts of the elements to be determined, to standard plutonium oxide sample (see 3.5.9.2), standard triuranium octoxide sample N.B.S. 95 - 1/7, and a (15 + 85) mixture of these oxides and carrying these standards through the entire procedure, including the corresponding sample preparation procedures.

### 3.5.9. Remarks

3.5.9.1. There is an influence of the nature and composition of the matrix on the form of the calibration graph. For this reason three different matrices are mentioned in this procedure, viz. plutonium oxide, triuranium octoxide and a (15 + 85) mixture thereof. The composition of the mixture has been chosen arbitrarily. However, for all practical purposes, calibration graphs drawn up with this mixture can be used for all compositions between 10 and 20 % of plutonium oxide. In the case that oxide mixtures of other compositions have to be analysed separate calibration graphs have to be constructed. It is also possible to dilute the sample with either standard plutonium oxide or standard triuranium octoxide so as to arrive at a composition (15 + 85). However, in this way the sensitivity of the method is reduced.

3.5.9.2. Pure plutonium oxide can be prepared by repeated purification of a plutonium nitrate solution in 7 M nitric acid on an anion exchange column, followed by a repeated precipitation as plutonium oxalate and dissolution in nitric acid, final precipitation and calcination at 500°C.

3.5.9.3. When silicon is not to be determined an **agate** mortar can be used.

TABLE 1  
Survey of methods for the chemical analysis of plutonium bearing non-irradiated nuclear fuels and their components

species or property to be determined	method	scope	precision	limit of detection	accuracy	standardization	interferences	application	procedure	references
Plutonium	Pu is oxidized to Pu(VI) with Ag(II). Excess Ag(II) is destroyed. Pu(VI) is reduced by Fe(II) and excess Fe(II) is titrated with Ce(IV). The equivalence point is indicated by constant current potentiometry	1 to 50 mg in about 50 ml	0.030 mg	0.1 mg	Application to NBS-Pu-sample 949 b yields results which do not differ significantly from the certified value	Ce(SO <sub>4</sub> ) <sub>2</sub> -solution is standardized against NBS-As <sub>2</sub> O <sub>3</sub> -sample	Mo, Mn, V, W and Ce interfere. However, usually the amounts present in Pu- and U-compounds are so small that their influence may be neglected	any Pu- solution in HNO <sub>3</sub> or H <sub>2</sub> SO <sub>4</sub>	B.1.1	A.5.3
	Pu is oxidized to Pu(VI) with Ag(II) in 4N HNO <sub>3</sub> . The absorbance of the solution is measured at 831 nm using a recording spectrophotometer with scale expansion facilities, readable slit width and 10 cm cells	0.02 to 7 mg in about 40 ml	<500 ug: 6.5 ug 500-7000 ug: precision varies from 9 to 120 ug coefficient of variation is about 1.8%	0.022 mg	NBS-Pu-sample 949 b is used for calibration	see accuracy	1.6 mmoles of PO <sub>4</sub> , 5 mmoles of SO <sub>4</sub> , 2 mmoles of F, 1000 mg of U, 5 mg of Mn, 350 mg of Ce and at least 15 mg of Th, Al, Co, Cr, Fe, Mo, Ni, V and Zr do not interfere. Cl, Br and J interfere	dilute Pu-solutions: small amounts of Pu in the presence of large amounts of U	B.1.2	A.5.4
URANIUM	U is reduced to U(IV) by Fe(II) in H <sub>3</sub> PO <sub>4</sub> -solution in presence of sulphamic acid. Excess Fe(II) is oxidized by HNO <sub>3</sub> in presence of Mo. U(IV) is titrated with K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> using Ba-diphenylamine sulphinate as an indicator	2 to 300 mg in maximum 15 ml	0.060 mg	0.2 mg	Application to NBS-UO <sub>2</sub> -sample 950 equilibrated with CO/CO <sub>2</sub> (see B.3.2) yields results which do not differ significantly from the calculated U-content	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> is a primary standard	Pu and Fe do not interfere. Neither interfere traces of impurities which are normally present in U- and Pu-compounds	any U-solution containing no more than 50 mmoles of NO <sub>3</sub>	B.1.3.	A.5.5.
PLUTONIUM AND URANIUM	After a pre-electrolysis of 0.5 M H <sub>2</sub> SO <sub>4</sub> on a mercury pool electrode at +0.1 V vs Ag-AgCl-electrode the sample is added and Pu(IV) is reduced to Pu(III). Next, U(VI) is reduced to U(IV) at -0.35 V	0.2 to 25 mg of Pu and 0.7 to 45 mg of U in maximum 10 ml	0.008 mg of plutonium 0.027 mg of uranium	0.027 mg of plutonium 0.089 mg of uranium	Results obtained do not differ significantly from those obtained with the volumetric methods mentioned above	Faraday's law	Ti(IV), Fe(III), W(VI), Mo(VI), V(V), Bi(III) and Cu(II) interfere. Usually the amounts present are so small that their influence may be neglected. NO <sub>3</sub> and Cl must be removed	NO <sub>3</sub> <sup>-</sup> and Cl <sup>-</sup> free Pu- and U-solution in H <sub>2</sub> SO <sub>4</sub>	B.1.4.	A.5.6.
OXYGEN TO METAL RATIO	The sample is weighed, oxidized with air (Pu <sub>2</sub> O <sub>7</sub> ) or equilibrated with CO/CO <sub>2</sub> (10:1) in the case of U- and U-Pu-oxides, both at 850°- 900°C and reweighed	PuO <sub>x</sub> : 1.5 < O/M < 2.0 UO <sub>2</sub> : 2.0 O/M < 2.67 (Pu,U)O <sub>x</sub> : 1.85 < O/M < 2.27 <sup>x</sup> and PuO <sub>2</sub> : 30%	0.0010	smallest detectable difference between samples is 0.0033	A (Pu,U) oxide equilibrated under the mentioned conditions is defined as stoichiometric	see accuracy	All metals or compounds which are oxidized or reduced under the conditions mentioned, interfere	PuO <sub>2-x</sub> UO <sub>2+x</sub> (U,Pu)O <sub>2+x</sub>	B.3.2	A.5.7 A.5.10
	Sample is dissolved in conc. H <sub>2</sub> PO <sub>4</sub> and U(VI) is reduced on a Hg electrode at -0.35 V vs Ag-AgCl-electrode. U(IV) is oxidized to U(VI) with K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> . Excess K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> is reduced at +0.1 V. Total uranium is then reduced at -0.35 V	UO <sub>2+x</sub> : 2.0 < O/M < 2.67	O/M=2-2.1: 0.0005 O/M>2.1: 0.0020	smallest detectable differences between samples are 0.0016 and 0.0065 respectively	Results do not differ significantly from those obtained by equilibration with CO/CO <sub>2</sub>	the coulomb is used as a primary standard	Ti, W, Mo, V, Bi and Cu interfere	UO <sub>2+x</sub>	B.3.3	A.5.8

Table 1 (continued)

Species or property to be determined	method	scope	precision	limit of detection	accuracy	standardization	interferences	application	procedure	references
water	Sample is heated under N <sub>2</sub> at 700°C and water vapour evolved is determined coulometrically	10 to 10000 µg	3.5 µg	12 µg	the method is calibrated with copper(II) sulphate penta hydrate	see accuracy	NH <sub>3</sub>	PuO <sub>2</sub> UO <sub>2</sub> (U,Pu)O <sub>2</sub>	B.3.4	A.5.9
carbon	Sample is heated in air and in oxygen. CO <sub>2</sub> is evolved and absorbed in NaOH-solution, the conductivity of which is measured before and after CO <sub>2</sub> -absorption	20 to 4000 µg	< 1000 µg : 7 µg > 1000 µg : 20 µg	23 µg	standard steel samples of Bundes-Anstalt für Materialprüfung are used for calibration	see accuracy	--	PuO <sub>2</sub> UO <sub>2</sub> (Pu,U)O <sub>2</sub> PuN UN <sup>2</sup> (Pu,U)N PuC UC (Pu,U)C Pu U Pu-U alloys	B.3.1	
silicon phosphorus aluminium iron magnesium manganese lead chromium tin nickel bismuth molybdenum * vanadium * copper silver * sodium * zinc	Sample is dissolved, the solution is evaporated to dryness and the residue calcinated. Ga <sub>2</sub> O <sub>3</sub> and traces of LOU (internal standard) are added and the emission spectrum is taken.  * the method is not applicable to the determination of these elements in plutonium oxide	10-300 ppm 15-500 15-500 2-100 1-50 5-100 1-50 5-100 1-50 5-50 15-100 1-50 0,2-5 30-400 30-500	15 %  (coefficient of variation)		NBS-samples 95-1/7, (U <sub>3</sub> O <sub>8</sub> ) and PuO <sub>2</sub> -samples, specially purified, to which known amounts of the elements are added, are used for calibration	see accuracy		PuO <sub>2</sub> U <sub>3</sub> O <sub>8</sub> (Pu,U)O <sub>2</sub> PuN UN <sup>2</sup> (Pu,U)N PuC UC (Pu,U)C Pu U Pu-U-alloys	B.3.5.	A.5.2

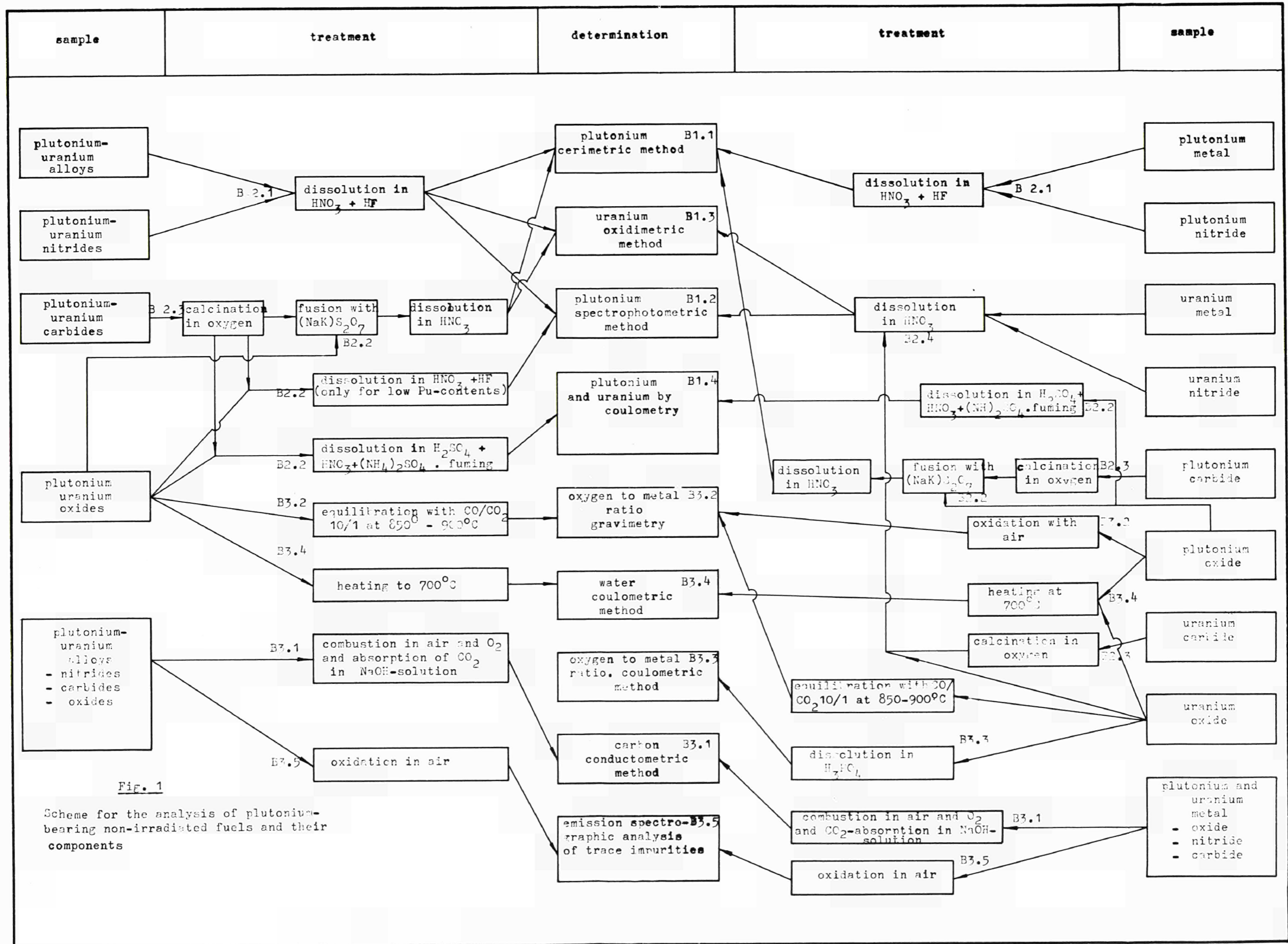


Fig. 1

Scheme for the analysis of plutonium-bearing non-irradiated fuels and their components



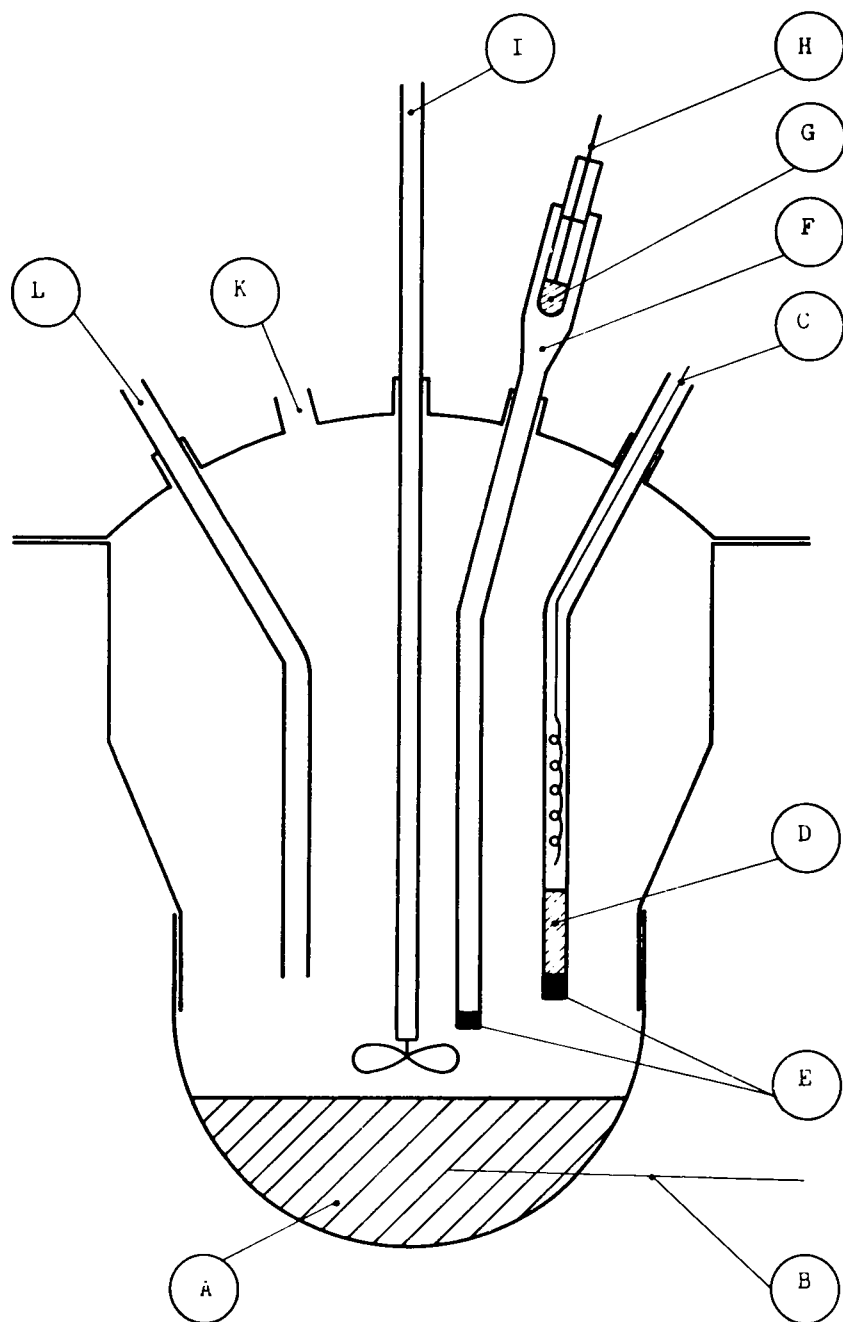


Fig. 5 Electrolysis cell  
 A mercury pool electrode  
 B platinum wire  
 C platinum wire helix  
 D  
 E sintered glass

F potassium chloride solution  
 G silver chloride  
 H silver wire  
 I stirrer  
 K sample addition  
 L nitrogen inlet

0 10 mm

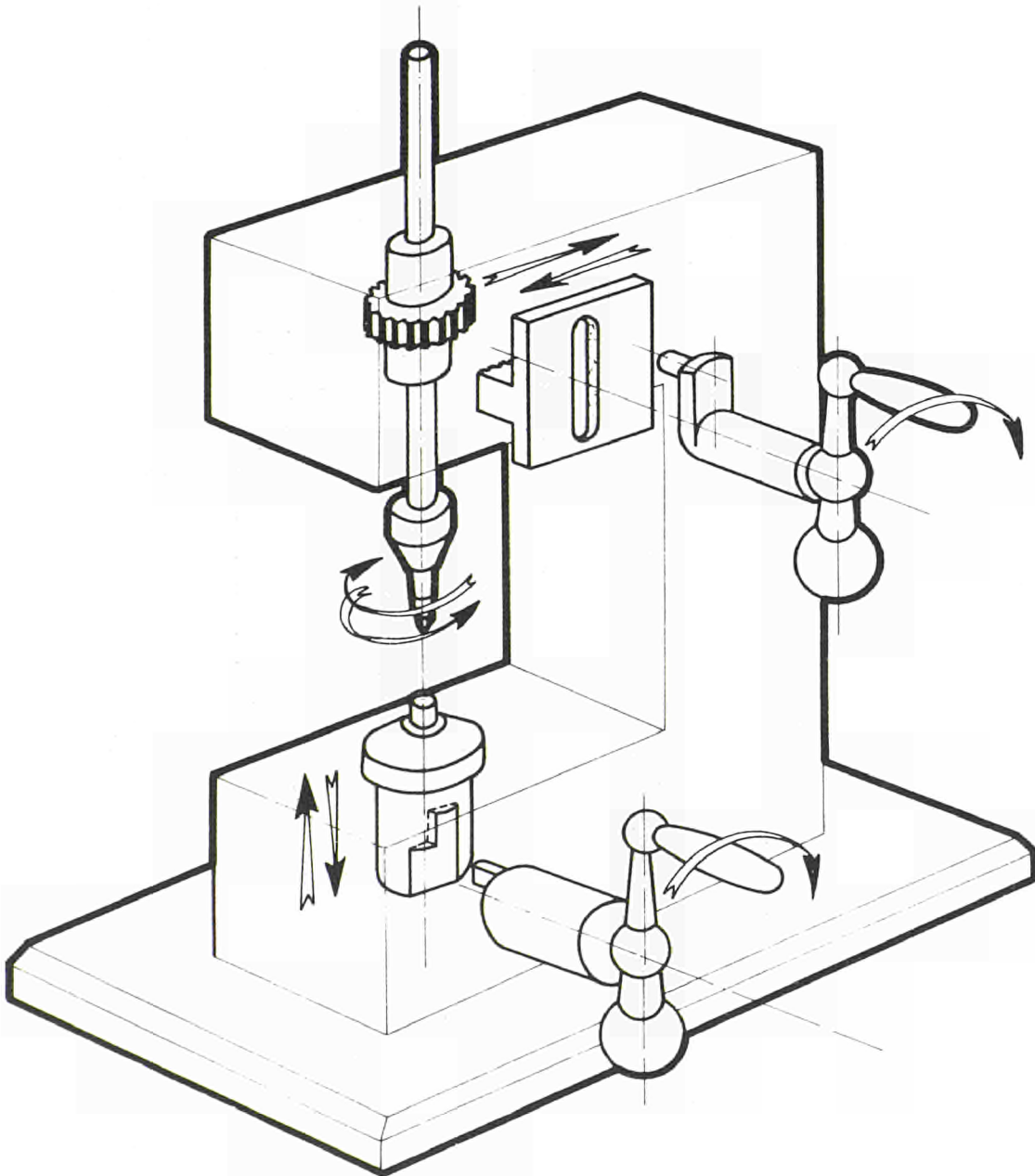


Fig. 4

Principle of the apparatus  
for the electrode preparation

0 20 40 60 mm



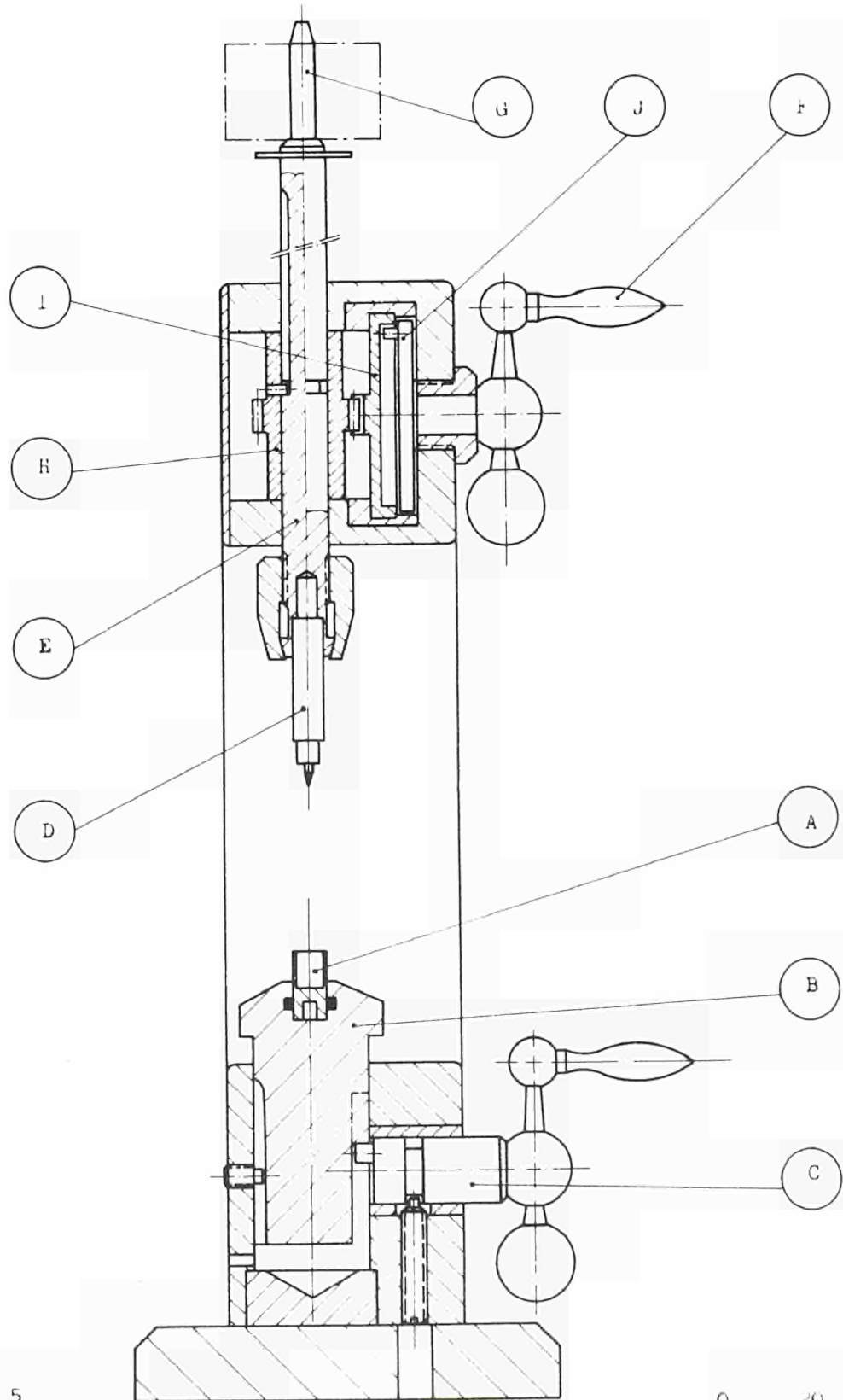


Fig. 5

- |                     |             |
|---------------------|-------------|
| A electrode holder  | F crank     |
| B shaker            | G weight    |
| C crank             | H pinion    |
| D vent-forming tool | I rack      |
| E rod               | J eccentric |

0 20 40 mm





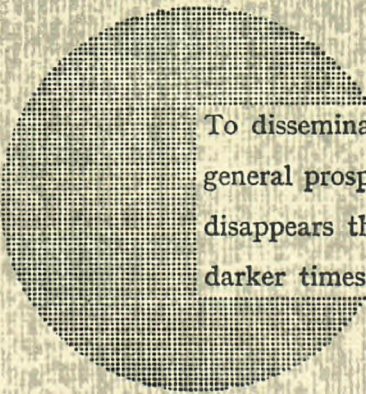
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Alfred Nobel



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