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GRAVIMETRIC DETERMINATION OF THE SUM OF URANIUM AND PLUTONIUM IN PRODUCTS OF THE URANIUM-PLUTONIUM-CARBIDE FABRICATION

by

L.M. ANGELETTI, W.J. BARTSCHER and J. REBIZANT

1971

Joint Nuclear Research Centre
Karlsruhe Establishment - Germany

European Institute for Transuranium Elements

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The standard deviation of the method is 0.035 %.

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ABSTRACT

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The standard deviation of the method is 0.035 %.

KEYWORDS

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URANIUM CARBIDES
PLUTONIUM CARBIDES
CARBON
AUTOMATION
OXIDATION
HEAT TREATMENTS
EFFICIENCY

Index *)

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1. Summary

A method for the gravimetric determination of the sum of uranium and plutonium in ternary mixtures of U_3O_8-PuO_2-C and in uranium-plutonium mixed carbides is described. The samples are oxidised in a current of air at 900°C and subsequently heated in a current of CO/CO_2 (10/1) in order to obtain the dioxides. The whole treatment is performed by an automated apparatus.

The standard deviation of the method is 0.035 %.

2. Introduction

Gravimetric analysis, based on weighing a product of well defined composition, free of impurities and stable in contact with the atmosphere, is one of the simplest and most precise methods used in analytical chemistry.

For the determination of uranium in uranium carbides the material is transformed into triuranium octoxide by heating in air [1]. This rather simple method is not applicable, however, in presence of plutonium, since in this case oxides of varying oxygen to metal ratio (depending on the plutonium concentration) are always obtained with an oxygen content below the theoretical composition U_3O_8+PuO_2 [2].

MARKIN and coworkers [3, 4] have demonstrated the possibility to transform mixed oxides of any composition ($MeO_{2\pm x}$) into a well defined composition ($MeO_{2.000}$) by equilibration in a CO/CO_2-atmosphere of definit oxygen partial pressure. They used this technique for the determination of the oxygen/metal ratio. In a recent paper an argon-hydrogen-water mixture is proposed for the same purpose [9]. We prefered the CO/CO_2-mixture because it is commercially available and no water adsorptions by the sample material are to be feared. Based on the statements of MARKIN and coworkers and using the technique of oxygen/metal determination, described in an earlier report [5], we elaborated a method for the determination of the two metals in oxide mixtures containing free carbon and in mixed carbides [(U,Pu)C].

3. Experimental part

3.1. Principles of the method

For the elimination of carbon the sample is heated for three hours in a current of air at 900°C.

The oxides so obtained are equilibrated in a current of CO/CO_2 (10/1) at the same temperature.

In order to avoid the formation of explosive gas mixtures the apparatus is flushed with argon prior to the introduction of the gas mixture.

In order to prevent a change of the equilibrium composition obtained at 900°C and to avoid any deposition of carbon on the sample the furnace is cooled under argon.

3.2. Apparatus

The scheme of the apparatus is shown in figure 1. After drying on molecular sieve and silicagel the air enters into the equilibrium furnace. To eliminate traces of reducing substances the argon passes through a furnace containing copperoxide at 600°C. Then, to absorb oxygen the gas passes through an other furnace containing copper turnings at 600°C. The CO/CO_2-mixture is also passed over the copper at 600°C to destroy carbonyls. The electric valves S_1-S_5 are opperated automatically by a devise consisting of an electric time switch for each gas and a system of relays. The whole apparatus is described in detail in another report [8].

3.3. Preliminary experiments

The accuracy of the results depends on the absence of elements other than uranium, plutonium and oxygen. Therefore, we studied the experimental conditions for the complete elimination of carbon, the extraneous element in our case. For reasons of simplicity and security we used air as an oxidant at the same temperatures (850° and 900°C) as usually applied for the equilibration of the oxides of uranium and plutonium. Quantities of about 400 mg of ternary mixtures (U_3O_8-PuO_2-C) or mixed carbides [(U,Pu)C] were treated under these conditions for three hours. In the residues of the oxidation the carbon was determined by the conductometric method [6].

The results are reported in table I. It can be seen that the combustion of carbon at 850°C is better for the ternary mixtures than for the carbides. This may be explained by the important difference in specific surface of the two products. The mixtures were fine powders, whereas the carbides consisted of pieces of about 1 mm in diameter. Furthermore it may be seen, that the treatment at 900°C gives lower and more reproducible results than that at 850°C. Consequently a temperature of 900°C was used in all further experiments.

Table I

Sample	Temperature (°C)	Number of Determinations	Residual carbon content (ppm)	
			Mean value	Standard deviation
U_3O_8-PuO_2-C	850	8	128	77
(U,Pu)C	850	8	355	252
(U,Pu)C	900	16	48	17

3.4. Procedure

- Weigh between 200 to 400 mg of sample material into a platinium crucible, which is 10 mm in height and 12 mm in diameter
- Put the crucible into another larger platinium crucible
- Put the crucibles on a quartz support
- Introduce the support into the cold furnace
- Switch on the timer, setting 4 hours for oxidation time, 0.5 hours for flushing time, 6 hours for equilibration time and a furnace temperature of 900°C
- After termination of the program extract the cold sample from the furnace

- Weigh the crucible containing the dioxides
- Calculate the result using the equation:

$$\% \text{ Me} = \frac{(P_2-P_o)-(t_2-t_1)}{P_1 - P_o} \cdot K$$

P_o = weight of the empty crucible
P_1 = weight of the crucible + sample
P_2 = weight of the crucible + dioxides
t_1 = weight of a platinium reference before treatment
t_2 = weight of a platinium reference after treatment
K = Conversion factor, depending on the average atomic weight ($\bar{A}$) of the metal mixture. $K=\bar{A}/\bar{A}+32.00$

3.5. Results

3.5.1. Determination of the precision

For the determination of the standard deviation of the method each of four specially homogenized samples of uranium carbide were analysed five times following the standard procedure. Comparing the obtained standard deviations by Bartlett's test [7] no significant difference was detectable on a level of probability of 0.05. Hence, a combined standard deviation was calculated. A value of 0.035 % was thus obtained for the standard deviation of a single result.

3.5.2. Ternary mixtures (U_3O_8-PuO_2-C)

The analytical examination was executed on two different batches of the same fabrication. From each batch ten samples were taken and analysed following the above procedure. The two standard deviations found did not differ significantly on a level of probability of 0.05 (F-test). So they could be combined thus giving a value of 0.058 %. If that value is compared with that obtained for the homogeneous uranium carbide, one observes a significant difference on a probability level of 0.05.

3.5.3. Mixed carbides [(U,Pu)C]

From one batch of mixed carbides five pellets were taken and each pellet was analysed twice. No significant difference on the 0.05-level was detectable between the standard deviations of the pellets and the batch. Hence all values could be combined to give a value of 0.060 %. This value differs significantly even on the 0.01-level from that obtained for the uranium carbide samples.

4. Discussion

Possible errors of the final result may derive from the following sources:

1. Residual carbon in the dioxide mixture
2. Presence of nonvolatile impurities in the residue of the treatment
3. Incertainty of the isotopic composition, i.e. the molecular weight of the dioxide residue
4. Incertainty of the oxygen/metal ratio of the residue.
5. Weighing errors.

The possible errors may be devided into two groups: systematic (1-2) and random errors (3-5). The accuracy of the results depends first of all on the content in nonvolatile impurities what may be seen already by the fact that usually the percentage in these impurities (~ 0.05 %) is higher than the standard deviation. However, if the content in impurities is known, corrections may be applied.

In order to get an estimation of the precision of the method, all random errors may be added statistically.

The molecular weight is known ~~up~~ to at least ± 0.1, thus yielding an error of $\pm 4.10^{-3}$ %.

The uncertainty in the oxygen/metal ratio is ± 0.003 [5] which leads to a possible error of ± 0.016 %.

The standard deviation for three weighings is ± 4.7 μg [5], which corresponds to $1.9 \cdot 10^{-3}$ % for a sample weight of 250 mg. The combined value of these random errors is $1.7 \cdot 10^{-2}$%. This value is much lower than the real standard deviation for the homogenized uranium carbide (3.5 . 10^{-2} %). This, and the fact that the values for the fabrication samples are higher than that for the uranium carbide, means that still other sources such as inhomogeneity of the sample material, sample losses during the treatment etc., contribute to the final standard deviation.

The high precision of the method and the facility of accurate carbon determination (s = 7 . 10^{-3} %) leads to the idea to calculate the percentage of volatile impurities in mixed carbides by taking the difference between the sum of plutonium, uranium, carbon and 100 %. Table II shows some results which were found on four samples belonging to the same batch in comparison to the results obtained by direct gas determination.

Table II

Sample	% gas calculated	% gas determined
1	0.33	0.21
2	0.23	0.30
3	0.35	0.44
4	0.34	0.49

On the other hand it should be possible to calculate the carbon concentration in U_3O_8-PuO_2-C mixtures if the oxygen concentration of the original products is known. In table III the values and standard deviations of two series, each consisting of ten samples and belonging to another batch are compared.

Table III

Batch	%C-calculated	Number of determinations	%C determined	Number of determinations
I	12.27 ± 0.07	10	12.05 ± 0.19	10
II	12.14 ± 0.06	10	12.28 ± 0.15	10

It is remarkable that the calculated values of the first batch are higher and those of the second batch lower than the corresponding values of the direct carbon determination. In both cases the differences are significant on the 0.05-level (t-test). This may be due to the following reasons: nonrepresentative sampling, variation of moisture content due to water absorption from the atmosphere.

5. Conclusions

1. The precision of the method, that is the standard deviation of a single measure, is 0.035 %
2. In the case of mixed carbides and if the concentration of carbon is known, an estimation of the percentage in volatile impurities is possible by a simple calculation.
3. If the oxygen concentration of the ternary mixture (U_3O_8-PuO_2-C) is known and if the fabrication is carried out under stable temperature and moisture conditions the method allows an estimation of the carbon concentration by simple calculation.
4. If a plutonium determination is effectuated on the sample the uranium concentration may be calculated by difference. The obtained values are as precise as those obtained by chemical analysis.

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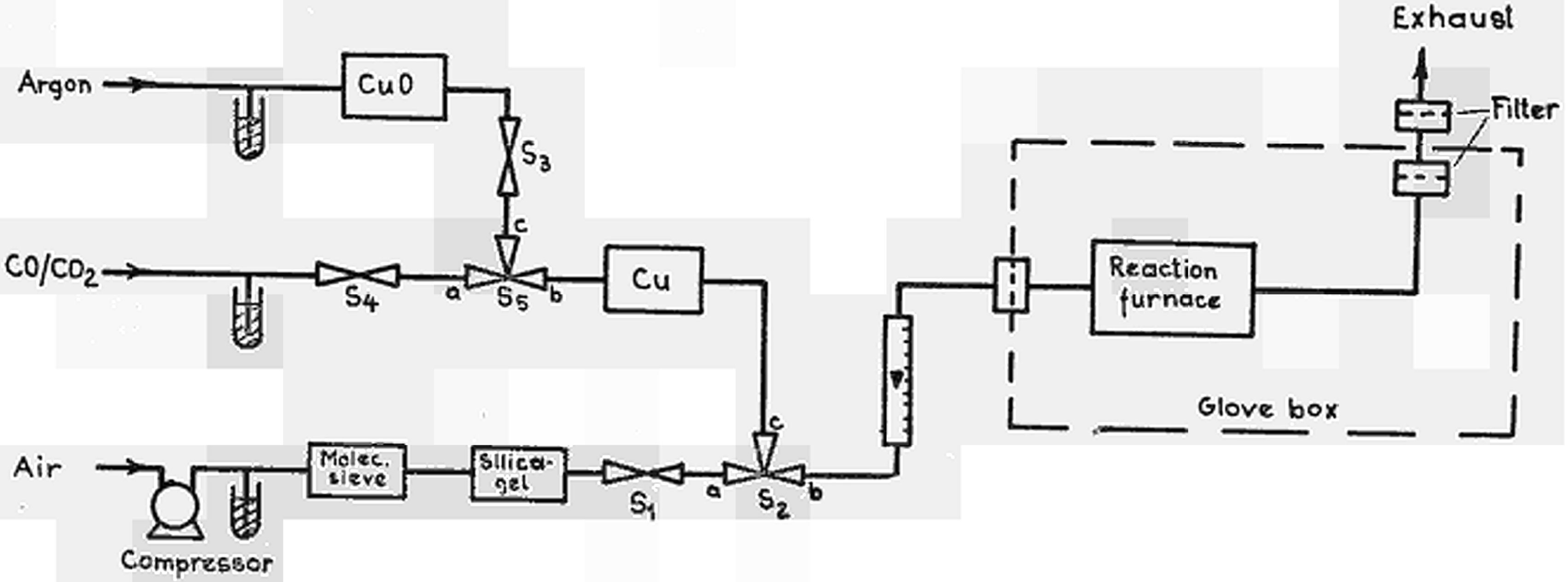
Argon
Cu0
S$_3$
c
CO/CO$_2$
S$_4$
a
S$_5$
b
Cu
Air
Compressor
Molec. sieve
Silica-gel
S$_1$
a
S$_2$
b
c
Exhaust
Filter
Reaction furnace
Glove box

Fig. 1

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