MASTER

ANALYSIS OF AMERICIUM BY CALORIMETRY

by

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RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

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ABSTRACT

A new method for the analysis of americium has been developed and is described in this report. The new method is based on the calorimetric measurement of the power emitted by the radioactive decay of americium-241 and correlating this measured power to the amount of americium in the sample. Experimental results show that the calorimetric method is more consistent and more accurate than the emission spectrographic method.

INTRODUCTION

The americium produced at Rocky Flats is presently analyzed by identification of the impurities by emission spectroscopy and subtracting the percent impurity from one hundred. This "by difference" method is not the best approach to an accurate americium analysis because it is not direct. However, since there is no known wet analytical technique for americium analysis, the "by difference" method has been used.

The new method described in this report is based on a correlation between the total heat released by decay of the radioactive material in the sample and the amount of radioactive material in the sample.

This calorimetric analytical technique for americium in bulk form has several advantages over the emission spectroscopy technique. These advantages will be discussed in this report. The results of this study show that calorimetric analysis of the americium oxide produced at Rocky Flats is feasible and the results obtained by calorimetry are more consistent and more accurate than the results obtained by the emission spectroscopic method.

EXPERIMENTAL

Emission spectroscopy is the current method of americium analysis. All the metal impurities are determined quantitatively by this method. These cation impurities are assumed to be in the form of the most stable oxide. The total percentage of oxide impurities is subtracted from one hundred to give the percent composition of americium oxide. The composition of the americium is assumed to be $\text{AmO}_{2.00}$ and the weight of americium is calculated accordingly. This "by difference" method of americium analysis is a standard method and therefore the details will not be discussed in this report.

The calorimetric method has been reported previously for the analysis of plutonium in plutonium dioxide.¹ The application of this method to americium differs from plutonium because the only power-emitting isotope is americium-241, whereas the material in plutonium analysis consists of 6 power-emitting isotopes. The operation and function of the calorimeter is the same as described previously. The instrument is a twin isothermal device involving a steady-state flow of heat from the power source (radioactive material) to a constant-temperature environment. The detection of heat flow is made by a Maier bridge in which two opposite arms detect the heat flow and two other arms are situated in the dummy or twin unit.

The americium samples weigh from 20 to 30 grams and have a power output of 2 to 3 watts. The sensitivity of the bridge is 2000 to 3000 microvolts per watt in this power range. The calorimeter is calibrated to an accuracy of ± 0.05 percent of a known electrical power.

A principle of the calorimetric technique is that a certain amount of radioactive material (americium-241, in this experiment) will emit a certain constant amount of heat per unit time. The heat per unit time is expressed conveniently in terms of power. By using the calorimeter to measure the total power emitted by a given americium sample, and by knowing the power emitted by a unit weight of americium, it is possible to calculate the amount of americium in the sample. The calorimetric analysis of americium involves the determination of the total power output of a given americium sample. The power output per unit weight of americium is a basic constant.

The power output per unit weight of americium-241 is related directly to the half-life. This is shown in the following expressions:

The decay of a radioactive substance is given by the expression:

$$-\frac{dN}{dt} = \lambda N \quad (1)$$

where $-dN/dt$ is the decay rate, λ is the decay constant and N is the number of atoms present. Upon integration of equation (1) where the constant of integration is evaluated from the limit $N = N_0$ when $t = 0$, equation (2) is derived:

$$N = N_0 e^{-\lambda t} \quad (2)$$

The half-life expression is derived from equation (2) by setting $t = t_{1/2}$, then $N = N_0/2$ which results in:

$$t_{1/2} = \frac{\ln 2}{\lambda} \quad (3)$$

By combining equations (1) and (3), thus eliminating λ , the following expression is derived:

$$t_{1/2} = \frac{N \ln 2}{-dN/dt} \quad (4)$$

which gives a direct relationship between the decay rate and the half-life.

The decay rate may be determined by dividing the power output of a given weight of americium-241, which is the energy per unit time of the total number of decays, by the energy evolved from a single decay of americium-241.

(1) F. L. Oetting, *J. Inorg. Nucl. Chem.* 27, 2151 (1965).

The energy of a single decay is taken from the work of Barenov, *et al.*,² who determined the alpha energy of americium-241 decay as 5.543 Mev. The recoil energy from the residual nucleus contributes 0.092 Mev and therefore the total energy per alpha disintegration becomes 5.635 Mev; or by converting to appropriate units, 9.0278×10^{-6} erg per atom.

The power output of a unit weight (one gram) of americium-241 is calculated to be 0.1080 watts per gram if the half-life of 458.0 years is used in the discussed calculation. This half-life value is based on two values given in the literature; 458.1 ± 0.5 years³ and 457.7 ± 1.8 years⁴ as determined by low geometry absolute alpha counting techniques. These values for the half-life are in disagreement with the calorimetric value of 432.5 ± 1.0 years⁵ which was derived from independent calorimetric measurements on two samples of high purity americium metal. The calorimetric half-life was derived from the power output measurement of 0.1145 watts per gram, which is considerably different from the power output of 0.1080 watts per gram derived from the specific activity half-life.

Since the calorimeter which had determined the power output of the two high-purity americium metal samples was also used for the americium analysis, the power value of 0.1145 watts per gram of americium-241 was used in the calculations in this study.

RESULTS AND DISCUSSION

In order to compare the calorimetric method to the emission spectroscopic method of analysis of americium, the following procedures were applied. Two independent analyses were taken on six samples of americium oxide by the emission spectroscopic method and the calorimetric method. The six samples originated from three independent batches of production material; two samples from each batch. From the 12 analytical results by each method, it was possible to ascertain any significant difference between two analyses of a sample by the same method, between the two methods on the same sample, and between the analyses of each batch.

The results of the experimental procedure are given in Table I. The three batches of americium are designated as 1, 2, and 3 and each batch is divided into A and B

TABLE I

RESULTS OF AMERICIUM ANALYSIS BY EMISSION SPECTROSCOPY AND CALORIMETRY

Batch	Sample	Weight (grams)	% Americium	
			Emission Spectroscopy	Calorimetric
1	1A	29.25	86.94	86.22
			86.63	86.09
			Avg. 86.78	Avg. 86.15
	1B	26.85	86.78	86.11
			87.00	86.00
			Avg. 86.89	Avg. 86.05
2	2A ^a	29.87	Assuming ^a	
			6% Ce	3% Ce
			77.90	81.12
			78.30	81.55
			Avg. 78.10	81.33
			Avg. 79.32	
	2B ^a	27.62	78.42	81.64
			78.20	81.46
			Avg. 78.31	81.55
			Avg. 79.19	
3	3A ^b	30.10	Assuming ^b	
			5% Ce	1% Ce
			81.06 ^c	85.38 ^c
	3B ^b	28.00	82.14 ^c	86.78 ^c

^a X-ray analysis determined Ce to be between 3 and 6%. The extremes of this range are considered.

^b X-ray analysis determined Ce to be between 1 and 5%. The extremes of this range are considered.

^c Duplicate emission spectroscopy results not obtained because of Ce uncertainty.

samples. On batch 2, x-ray analysis reported a cerium content between 3 and 6 percent. The results are reported assuming the extremes of this range. Similarly with batch 3, the cerium was reported between 1 and 5 percent and the extremes of this range are considered.

The statistical conclusions regarding the comparison of calorimetric with emission spectroscopic analysis of americium are summarized in the following discussion. All statistical tests were made at the 95 percent confidence level.

- Analyses of batch one show that there are significant differences between the results obtained from the two methods; emission spectroscopy and calorimetry. The mean of the emission spectroscopy results is 86.84 percent. The mean of the calorimetric results is 86.10 percent. The analytical

(2) S. A. Barenov, U. M. Koulakov, A. G. Zelenkov, and V. M. Chatinski, *Zhur. Eksp. Teor. Fiz.* 43, 795 (1962); see also *Nucl. Phys.* 43, 547 (1963).

(3) G. R. Hall and T. L. Markin, *J. Inorg. Nucl. Chem.* 4, 137 (1957).

(4) J. C. Wallmann, P. Graf, and L. J. Goda, *Inorg. Nucl. Chem.* 7, 199 (1958).

(5) S. R. Gunn and F. L. Oetting, to be published.

results from batches two and three were not statistically tested because the emission spectroscopy method cannot be used accurately to determine the cerium content above one percent. This severely limits the use of the emission spectroscopy method. In batch one the cerium content was below one percent. The results from the averages of the two methods show a difference of 0.74 percent.

- Referring only to the calorimetric results, statistical analysis shows no significant difference between sample means of batches one and two. The standard deviation between sample means for these two batches is 0.07 percent. Inclusion of batch three into the statistical computation shows that there is a significant difference between sample means for each batch. The standard deviation between sample means is 0.21 percent when all batches are considered. This standard deviation is considerably larger than the standard deviation between sample means of batches one and two.

It is difficult to perceive that the significant difference between sample means, when all three batches are included, is real, however. It is evident that the significant difference between sample means for all batches is caused by the comparatively large deviation in sample means of batch three. It is quite possible that the wide deviation between sample means in batch three is not caused by the analytical behavior but by sampling procedure, e.g., inhomogeneity of the sample. This implication of no erratic analytical behavior arises from the fact that there was no irregularity in the calorimetric behavior on sample three. The implication that inhomogeneity was present in the batch is substantiated by the results of emission spectroscopy on samples 3A and 3B which indicate a comparatively large difference in americium content between the two samples. Neither method indicates large differences in americium content in either samples 1A and 1B, or samples 2A and 2B.

- The analytical standard deviation for the calorimeter method is 0.05 percent americium. Based on results from all three batches, the relative analytical standard deviation is 0.06 percent. The standard deviation for the emission spectroscopy method was not calculated between the americium results in batches two and three are dependent upon the x-ray analysis of cerium of between 3 and 6 percent in batch two and between 1 and 5 percent in batch three.

CONCLUSIONS

The statistical results show that the calorimeter has a precision of better than ± 0.1 percent for americium determinations. This compares to the precision of the emission spectroscopy method of between 3 and 4 percent when the cerium content is above one percent; however, the precision of the emission spectroscopy method is comparable to the calorimetric method when the cerium content is below one percent.

The accuracy of the calorimetric method of determination of americium is ± 0.2 percent. This value is based on the error of the power output to ± 0.1 percent and the accuracy of the method to ± 0.1 percent.

The latter is based on the results of the analysis of plutonium in plutonium dioxide.¹ The accuracy of the americium content as determined by emission spectroscopy is unknown because of the assumptions made. The most severe assumptions are that all impurities are present as their most stable oxides and the americium is presumed to exist in the form of $\text{AmO}_{2.00}$. It is not known whether or not $\text{AmO}_{2.00}$ is a stoichiometric compound.

Insufficient data were obtained to determine absolutely which method is more accurate. Because of the assumptions and methods necessary for emission spectroscopy (all impurities are in the form of stable oxides, analysis of cations only, subtraction from one hundred, the uncertainty in the cerium content, and the greater significant difference in the analysis), it appears that the calorimetric method is more accurate. There is no known reliable wet analytical technique for americium analysis which would verify this conclusion. A significant advantage is that calorimetry is a direct and absolute method.

The calorimetric method also has the advantage of analyzing the batch as an entire unit instead of relying upon the analysis from a small portion of the batch. The portion removed for emission spectroscopic analysis is assumed to represent the entire batch; however, in actuality this may not be a truly representative sample of the entire batch.

Another distinct advantage of the calorimetric method in the quantitative determination of any radioactive

(1) F. L. Oetting, *loc. cit.*, p 1.

material is that there is a minimum of handling of the material. In this study, the cans which are used to encapsulate the americium material for calorimetry are also the containers used for shipping.

Another advantage is that the calorimetric method is a nondestructive method of analysis. This is an important consideration because some radioactive materials cost thousands of dollars per gram.

There are disadvantages of the calorimetric technique. If there are any unknown radioactive isotopes in the

sample, the calorimeter analytical value will be in error. If the amount and power output of any foreign isotope are known, the americium result can be corrected. The calorimetric method determines only the americium-241 content and consequently does not give the impurities. The impurities, however, are obtained from the emission spectroscopy results.

It is concluded from this study that the calorimetric method, when compared with the spectroscopic method obtains more consistent and more accurate analytical results for the americium content in the sample.