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LOS ALAMOS SCIENTIFIC LABORATORY
OF THE UNIVERSITY OF CALIFORNIA ○ LOS ALAMOS NEW MEXICO

SPECTROPHOTOMETRIC DETERMINATION OF MICRO QUANTITIES OF CHLORIDE IN PLUTONIUM METAL

Printed in USA. Price $ .50. Available from the

Office of Technical Services
U. S. Department of Commerce
Washington 25, D. C.

LA-2921
UC-4, CHEMISTRY
TID-4500 (21st Ed.)

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REPORT WRITTEN: May 1963

REPORT DISTRIBUTED: September 9, 1963

SPECTROPHOTOMETRIC DETERMINATION OF MICRO QUANTITIES OF CHLORIDE IN PLUTONIUM METAL

by

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Contract W-7405-ENG. 36 with the U. S. Atomic Energy Commission

ABSTRACT

Micro quantities of chloride are determined spectrophotometrically after separation from plutonium metal by pyrohydrolysis. Complete separations are accomplished by heating samples of plutonium metal at 900 to 1000° C. in a stream of argon initially saturated with water at 85° C. The gas stream sweeps the trace element, as hydrogen chloride, into an alkaline absorbing solution. Reagents are added to form colored ferric thiocyanate complex in an amount equivalent to the chloride, and concentration of the complex is determined spectrophotometrically as an indirect measurement of chloride. Optimum range of chloride concentration in analyzing 1-gram plutonium samples by this method is 10 to 50 p. p. m., with relative standard deviations of 12 and 8 percent, respectively. The range can be extended to 5 and 200 p. p. m. by modifying sample size. Iodide, bromide, cyanide, and thiocyanate interfere in this spectrophotometric chloride method, but these ions normally are not present after a pyrohydrolytic separation.

INTRODUCTION

A rapid, reasonably accurate and precise analytical method was required for the determination of trace amounts of chloride in plutonium. In analysis of other metals for micro quantities of chloride, frequently the sample is dissolved in an appropriate acid, and chloride in the resulting solution is measured by one of the many available methods. This approach has certain disadvantages when applied to plutonium, such as the potential hazards of making measurements in a radioactive solution. In addition, the usual reagent for convenient, rapid dissolution of plutonium, hydrochloric acid, obviously can not be used. To avoid these disadvantages, pyrohydrolysis was selected as a method for initially separating traces of chloride from samples of plutonium.

Pyrohydrolytic separations have been employed successfully in analytical methods for both fluoride(2, 6, 9) and chloride.(5) Samples placed in a suitable apparatus are maintained at an elevated temperature, as high as 1000° C., and simultaneously exposed to a stream of superheated steam. The collected condensed steam contains all of the separated hydrogen halide, but metal components of the sample are retained as oxides in the original sample container. With some samples the separation can be improved by using a mixture of steam and air or oxygen. Generally, the release of a hydrogen halide from a light-metal compound requires an initial mixing of the sample with an accelerator; uranium, tungsten, or chromium oxide have been used for this purpose.(1, 2) Both macro and micro amounts of fluoride(8) have been quantitatively separated from samples by pyrohydrolysis.

After this separation of chloride into an essentially non-radioactive solution, it was proposed tentatively to complete the analysis with a simple, rapid spectrophotometric determination(3, 7) in which a quantity of red ferric thiocyanate complex equivalent to the separated chloride is formed and measured.

EXPERIMENTAL WORK

Separation by Pyrohydrolysis

Initial experiments with pyrohydrolytic chloride separations were made with oxygen saturated with water at room temperature as the carrier gas. This combination was used in place of steam to restrict the volume of liquid in which the chloride would be collected. The gas stream coming from the pyrohydrolysis tube was bubbled through 20 ml. of dilute alkaline-absorbing solution to collect hydrogen chloride. These conditions permitted the addition of required reagents and dilution to a final volume, not greater than 25 ml., before the spectrophotometric measurement was completed. Mixtures of known, micro quantities of sodium chloride and 1-gram portions of uranium oxide (U_3O_8) were used to evaluate the chloride recovery for this separation procedure. Results were uniformly low with an average recovery of 70%.

These incomplete recoveries may have been caused by the oxygen gas which was used for pyrohydrolysis. If there is a partial conversion of chloride by oxygen to an oxidation state which is above that in chloride, low results would be observed because the spectrophotometric method employed is sensitive only to chloride. Consequently, a change was made to an inert carrier gas, argon. At the same time the relative proportion of steam was increased by saturating the argon with water at 85° C. instead of room temperature before the gas entered the pyrohydrolysis tube. After these changes in conditions were made the recoveries for known amounts of sodium chloride mixed with uranium oxide were consistently in the range of 100 ± 10%. The time required for complete separation of chloride was relatively short (10 to 15 minutes), and the volume of condensed steam collected in the alkaline absorbing solution was small enough to continue with the process of diluting to a final volume of 25 ml.

Standard Samples

Samples of plutonium metal containing known, trace amounts of chloride were not available. Therefore, attempts were made to introduce known amounts of chloride into plutonium metal. The first experiments to produce a standard sample involved use of a modified Conway diffusion cell.(4) Plutonium metal turnings contained in a quartz boat were placed in one compartment of the cell. In the other compartment were potassium permanganate and sulfuric acid to which a known amount of chloride had been added. After the cell was sealed, the permanganate and acid were mixed, but without direct contact with plutonium. Presumably, the chlorine from the two mixed reagents would react completely with plutonium metal and yield a known chloride sample. When these standard samples were used for pyrohydrolytic separation and subsequent chloride determinations, the percent recovery of chloride was generally between 50 and 75%. Modifications in sample preparation were made without improvement in recovery. It was concluded that the plutonium chloride formed in the cell probably undergoes partial hydrolysis. Some of the hydrogen chloride thus formed collects on the inside surface of the cell and remains out of contact with either the metal or the oxidizing solution in the two cell compartments.

It was decided finally to use a mixture of plutonium dioxide and sodium chloride prepared in the following manner. High-purity plutonium metal was converted to oxide by pyrohydrolysis under the conditions normally used for chloride separation. A 1-gram portion of this oxide was placed in a quartz boat and then a measured volume of known sodium chloride solution was added as uniformly as possible. The maximum volume of added chloride solution was limited to 50 microliters. After standing at room temperature to allow evaporation of most of the added water, the quartz boat was transferred to the pyrohydrolysis apparatus for chloride separation and determination. The recovery of chloride from this material was similar to that which was observed with mixtures of sodium chloride and uranium oxide. Various mixtures of sodium chloride and plutonium oxide were used in estimating the reliability of the recommended method.

APPARATUS AND REAGENTS

Apparatus

Balance, analytical. Ainsworth Model BCT.

Boat, quartz, 10 x 50-mm.

Flask, volumetric, 25-ml.

Flowmeter, Fischer and Porter Co., Catalog No. 448-100. This instrument is used to measure flow of argon gas before saturation with water and passage through the pyrohydrolysis tube. (See Fig. 1 for arrangement of equipment).

Furnace, Hevi Duty Electric Co., Multiple Unit Type 122 H-2, 512 watts, or equivalent, equipped with thermocouple to measure temperature.

Inner sleeve, quartz, for pyrohydrolysis tube, 90-mm. length and 16-mm. outside diameter. This sleeve is convenient for rapid insertion of the quartz boat into the heating zone of the pyrohydrolysis tube and also protects the tube from accidental damage caused by hot plutonium metal. A heavy nichrome wire can be used in moving the sleeve in or out of the tube.

Test tube, borosilicate glass, 20 x 150-mm.

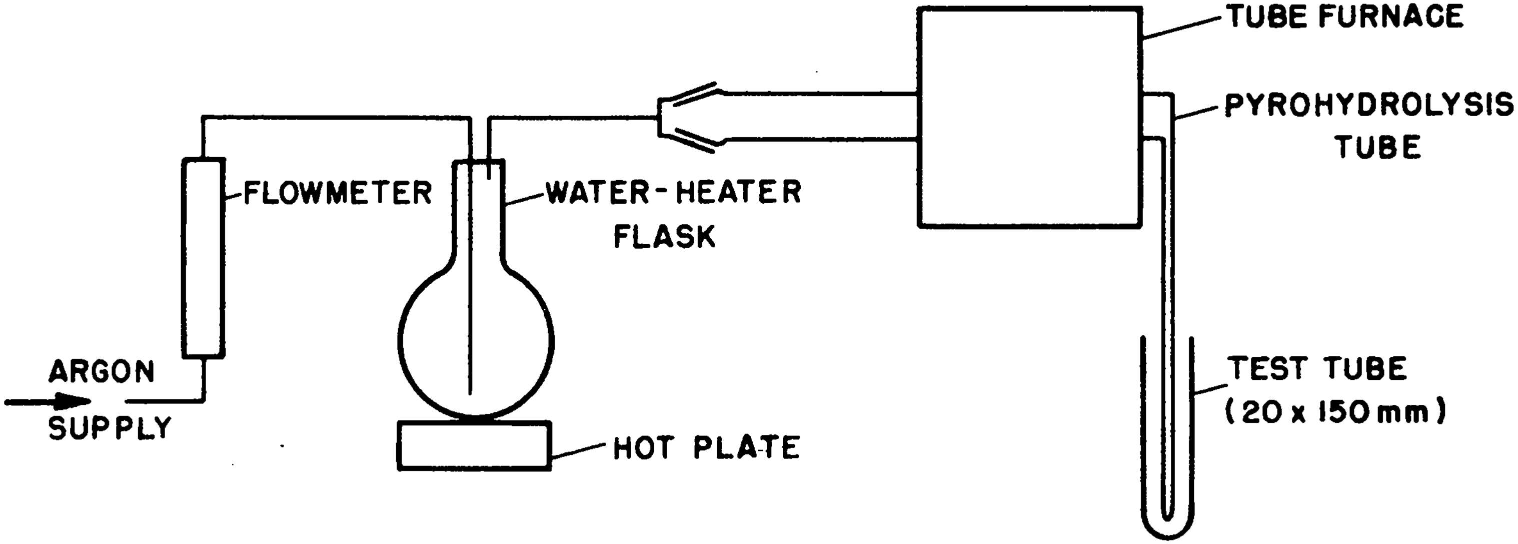

Fig. 1. Apparatus for Chloride Separation by Pyrohydrolysis

Tube, pyrohydrolysis, quartz. The main section of this tube is 20 mm. in outside diameter and 35 cm. in length, including a 24/40 ₸ inner joint sealed to the entrance end of the tube. The opposite, rounded test tube end is sealed to a 7 x 240-mm. exit tube so that the two tubes are at right angles. The open end of the exit tube is reduced to a tip with a bore between 0.5 and 1.0 mm. This pyrohydrolysis tube is placed in the furnace in such a position that the 7-mm. exit section is vertical, pointing downward, and is separated about 1 cm. from one of the flat ends of the furnace. Asbestos tape can be used to fit the 20-mm. tube tightly in the furnace openings. A 24/40 ₸ outer joint is used as a cap to close the pyrohydrolysis tube. The tubing end of this 24/40 outer joint is reduced in diameter to 7 mm. to permit connection between the cap and supply of saturated argon gas with gum rubber tubing.

Water-heater flask, borosilicate glass. Water in a 1-liter flask is maintained at 85° C., with an adjustable electric hot plate. The flask has glass and gum rubber tubing connections to permit the flow of argon gas to bubble through the heated water and then into the pyrohydrolysis tube.

Reagents

Argon gas

Ferric ammonium sulfate, 0.25 M in 9 N nitric acid, analytical reagent grade.

Mercuric thiocyanate solution, saturated, in 95% ethanol.

Phenolphthalein indicator solution, 0.1% in 90% ethanol.

Plutonium dioxide, chloride-free.

Sodium chloride, analytical reagent grade.

Sodium hydroxide, 0.05 N, analytical reagent grade, in polyethylene dropping bottle.

RECOMMENDED PROCEDURE

Analysis of Sample

Prepare the pyrohydrolysis apparatus for use as follows: (a) allow the tube furnace to come to a temperature in the range of 900 to 1000°C., (b) adjust the water temperature in the water-heater flask to 85° C., (c) maintain the argon flow between 150 and 175 ml. per minute, (d) add about 19 ml. of distilled water to each 20 x 150-mm. test tube (one required for each sample or blank determination) along with one drop of phenolphthalein solution and 6 or 7 drops of 0.05 N sodium hydroxide. Disconnect the 24/40 ₮ cap from the pyrohydrolysis tube. Place one of the prepared 20 x 150-mm. test tubes so that the tip of the exit tube is immersed in the dilute alkaline solution at a level just above the test tube bottom. (Note: if the indicator in the test tube turns colorless at any time, adjust to alkaline condition with additional drops of 0.05 N sodium hydroxide).

Transfer a 1-gram sample of plutonium to a quartz boat. Place a quartz inner sleeve just into the pyrohydrolysis tube and then put the boat into the sleeve. Rapidly move the sleeve and boat into the maximum temperature section of the tube and immediately replace the cap on the tube. Continue heating the sample with uniform gas flow for 15 minutes. Then remove the 20 x 150-mm. test tube and quickly replace it with another test tube containing water, indicator and sodium hydroxide. Continue heating and gas flow for 15 minutes with the second test tube which will be used subsequently for a blank determination. At the end of the second heating period, remove the test tube, disconnect the cap, and withdraw the quartz inner sleeve and boat. After cooling, the contents of the boat may be transferred to a residue bottle reserved for this material.

Transfer the solution from each 20 x 150-mm. test tube to a separate 25-ml. volumetric flask and, if necessary, cool to room temperature. Add 2 ml. of ferric ammonium sulfate solution and 2 ml. of mercuric thiocyanate solution. Mix the contents of the flask, add distilled water to the mark, and again mix the contents thoroughly. Allow the solution in the flask to stand for 10 minutes. Then transfer a portion from each 25-ml. flask into separate, clean, dry, 1-cm. Corex cells. Without delay, determine the absorbance for each solution at 460 millimicrons, using distilled water as a reference liquid. The net absorbance reading, corresponding to the chloride in the sample, is obtained by subtracting the reading for the second (blank) solution from the reading for the first solution.

Calibration Curve

Prepare a standard sodium chloride solution which contains 1 microgram of chloride per microliter. Place 1-gram portions of chloride-free plutonium dioxide in quartz boats and add a separate aliquot of standard chloride solution to each portion of oxide. The solution should be added as uniformly as possible and should wet only the plutonium oxide and not the boat. Allow the mixture to stand until moisture is lost by evaporation. Then transfer the quartz boat to the pyrohydrolysis apparatus, following directions given under Analysis of Sample. Use a 1-gram portion of plutonium oxide, without addition of any sodium chloride, in a separate quartz boat for a blank determination. Prepare a calibration curve by plotting weight of chloride versus difference between absorbance reading for sample containing sodium chloride aliquot and absorbance reading for blank determination.

RELIABILITY OF THE METHOD

Reliability of this method was estimated by repeated analyses of control samples, prepared from chloride-free plutonium oxide and analytical reagent sodium chloride. The volume of standard chloride solution was limited to a maximum of 50 microliters to avoid spreading any of the sodium chloride out of contact with the plutonium oxide. At each concentration level 13 samples were analyzed. In the range of 10 to 50 micrograms of chloride, or 10 to 50 p.p.m. for 1-gram samples, the relative standard deviation varied from 12 to 8%, respectively. If these chloride determinations were repeated with sodium chloride aliquots added directly to 25-ml. flasks and, therefore, without a separation by pyrohydrolysis, the corresponding relative standard deviations were 1.6 and 1.0%, but the calibration curve remained essentially unchanged. It was concluded that the recommended separation by pyrohydrolysis, within the range of 10 to 50 micrograms of chloride, does not affect the accuracy of chloride measurements significantly, but it does decrease the precision of measurements. The recommended method can be used for samples containing from 5 to 200 micrograms of chloride, but the relation between amount of chloride and net absorbance reading from the spectrophotometric determination is not entirely linear for samples containing more than 50 micrograms. Interference from iodide, bromide, cyanide, or thiocyanate ions, normally observed for this spectrophotometric determination, is not significant when plutonium samples are subjected to a chloride separation by pyrohydrolysis.

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