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Sealed-Tube Dissolution Method with Applications to Plutonium-Containing Materials

by

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ABSTRACT

Experience with a previously known technique for dissolving highly refractory materials is described. This technique, which seems to have been overlooked by most laboratories, has been found to have wide application. It consists of sealing the sample with hydrochloric acid and an oxidant in a heavy-walled silica tube and heating to a suitable temperature, usually between 100 and 350° C. The sealed silica tube is first placed in a steel shell to which solid carbon dioxide is added to compensate for the high internal pressure generated in the tube. Application of this dissolution method to refractory plutonium-containing materials is described in detail.

ACKNOWLEDGMENTS

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INTRODUCTION

The sealed-tube method, as described by Wichers et al.[1, 4] of the National Bureau of Standards in 1944, has been in active use in our laboratories since that time to dissolve various refractory materials. The original paper that appeared in the Journal of Research of the National Bureau of Standards apparently did not have wide circulation. The large number of requests received by this Laboratory for information of this type indicates that the sealed-tube method remains to be discovered by many analysts. Few references to this method have been made in the open literature; one recent exception briefly reviews several of the high temperature.high pressure decomposition methods as an introduction to a description of a platinum-lined vessel for dissolving silicates in hydrofluoric acid.[2] However, in general, the sealed-tube dissolution method seems to be little known, and this report is being written to disseminate more widely the information about the method and to describe the modifications made at this Laboratory to accommodate plutonium-containing materials.

During the past 20 years great interest in the physical and chemical properties of refractory materials, both ceramic and cermet in nature, has developed. Of particular significance is the increased interest in such materials having high purities and well established compositions. As a result of this interest, increased emphasis has been placed on precise analyses and measurements of many impurities in the low parts-per-million range. Thus the need has arisen for dissolving techniques that permit more precise analyses of these materials, and in many cases, techniques that do not add impurities even in trace amounts.

While methods for dissolving refractory materials have existed for many years, many, such as high-temperature alkali fusions, fusions with various salts and mixtures of salts, and prolonged refluxing with various acid mixtures, often produce solutions that do not lend themselves to subsequent precise analyses for main constituents or to the determination of trace impurities. Development of the sealed-tube method by Wichers et al. permitted the relatively rapid dissolution of noble metals and many refractory compounds without the disadvantages of the other methods. A "clean" hydrochloric acid solution of the sample was obtained, the only contaminant being silica.

The sealed-tube method is applicable to dissolution of many materials that are essentially insoluble in hydrochloric acid at temperatures limited by the boiling point of the acid solution at atmospheric pressure. The rate of dissolving is greatly increased by sealing the sample, acid, and an oxidant into a glass, or, preferably, fused-silica, tube and heating at temperatures above the normal boiling point of the acid. In many cases the pressure developed by the acid mixture at the elevated temperature is as much as 4000 psi. Therefore, the sealed tube is enclosed in a steel shell along with a calculated amount of solid carbon dioxide that develops a pressure in the heated shell to compensate for the high internal pressure in the tube.[1, 4]

The method is restricted to materials and solvents that do not react appreciably with glass or fused silica at elevated temperatures. If part of the sample will react with the solvent at room temperature, this reaction is allowed to proceed before the sample and acid are sealed in the tube. For large samples, only the insoluble residue remaining after the initial acid attack is placed in the tube. The method has been applied to refractory oxides including high-fired magnesia and sintered plutonia, many ceramic materials, platiniferous materials, rhenium alloys of tungsten and molybdenum, and plutonium alloys containing ruthenium

and several other metals. Various plutonium carbides and nitrides, following ignition in oxygen to plutonia, also have been dissolved in this manner. However, samples that contain even small quantities of organic material should not be dissolved directly by the sealed-tube method if either perchloric acid or sodium chlorate is added as the oxidizing agent.

APPARATUS AND REAGENTS

Apparatus

The potential hazards involved with equipment under high pressure and with radioactive materials require that great care be exercised and that suitable equipment be used. The necessary equipment includes glove boxes for handling plutonium, usual laboratory equipment, and the following special items.

Oven, electric, adjustable within ±5° C in the 150 to 350° C range. The oven in which plutonium-containing materials are heated should be inside a glove box to contain radioactive contamination if the sealed tube ruptures.

Steel shell and nut.[1,4] This equipment is illustrated in Fig. 1. Items needed for handling the steel shell include annealed copper gaskets, a support to hold the shell rigidly, and a wrench to fit the 2-in. steel nut. An 18-in. adjustable wrench is satisfactory.

Accessories for steel shell. A pellet, 3/4 in. in diam. and 3/8-in. thick, made by pressing about 5 grams of finely powdered calcium carbonate, is enclosed in the small metal can (Fig. 2) that has several small openings in the bottom which are covered with a thin layer of glass wool. The encapsulated pellet is placed in the bottom of the steel shell, and a thin-walled metal cup, which has an i. d. of 7/8 in., a perforated bottom, and a top flared to 15/16-in. diam., is placed on top of the pellet. The can and cup may be fabricated from any suitable material such as copper, brass, or steel, but should not contain soft-soldered joints. A transparent, poly methyl methacrylate tube, having an o. d. of 7/8 in., a wall thickness of 1/8 in., and one sealed end, is constructed with an inside bevel on the open end. This bevel allows the plastic tube to slide easily over a fused-silica or glass tube in the shell. The plastic tube makes a snug slip-fit in the cup which closes the tube and supports the quartz tube during its removal from the shell. The plastic tube and cup are shown in Fig. 2.

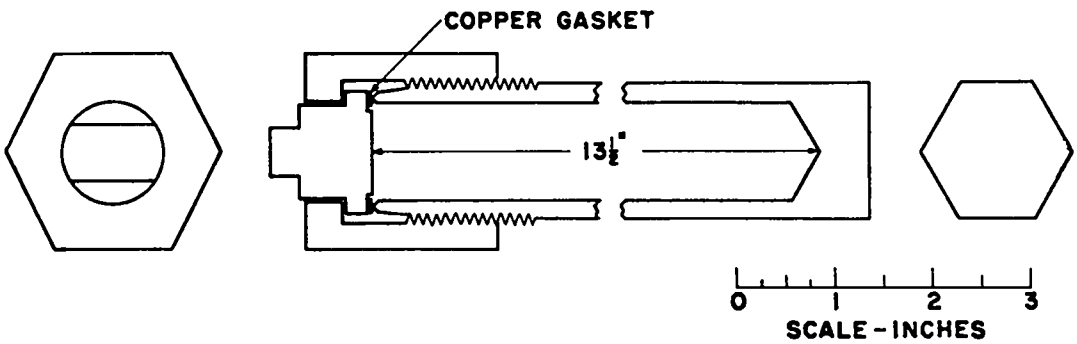

Fig. 1. Steel shell for protection of sealed tube.

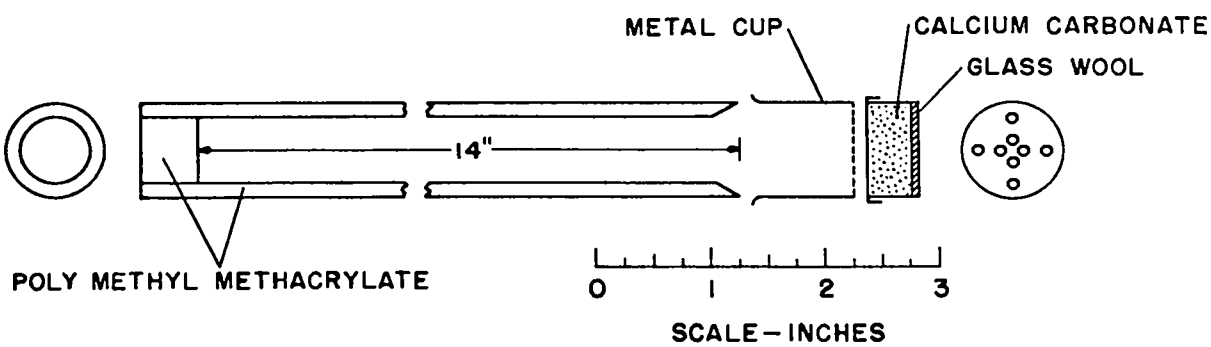

Fig. 2. Special accessories for the steel shell.

Transfer unit, consisting of a metal can, approximately 4 in. in diam. and 6-in. high, with an 8-in.-high cover of the same diam. which is held in place by three fasteners of the suit-case catch type. The top of the cover contains perforations which are covered by a baffle plate approximately 1/4 in. below the top.

Tube, glass, 34-cm. long, 16- to 18-mm. i. d., with one end sealed. This tube is used to hold and prevent contamination of the fused-silica tube during the addition of the sample and acid. (Used only for plutonium-containing materials).

Tubes, heavy-wall, fused-silica or glass, approximately 8-mm. bore, 2-mm. wall thickness, 38-mm. (15-in.) long, one end sealed. The maximum length for a tube after sealing is about 30 cm. (12 in.).

Tubes with a bore no greater than 4 mm. and a wall thickness no less than one-half of the bore can be used in this procedure without being secured in a tightly closed steel shell. They should be placed in a piece of pipe with loosely fitting screw caps that will serve to keep glass from scattering in the event of a failure. Tubes with a bore between 4 and 8 mm. and a wall thickness no less than 2 mm. can be sealed successfully, but sealing becomes considerably more difficult with larger tubes. If the bore is between 8 and 15 mm., the wall thickness should be between 2 and 3 mm. Also, the larger tubing must have a sealing stem attached to it before the insertion of any sample. The sealing stem should have a bore which is as small as possible, not larger than 8 mm.

Fused-silica tubing of this type is available from the General Electric Company and other suppliers in 15- and 30-in. lengths. Tubes 15-in. long are prepared from the General Electric tubing by sealing one end.

Reagents

Hydrochloric acid, 36%, reagent grade. At times it may be desirable to use more dilute or more concentrated acid. The latter, up to about 45 wt. %, may be prepared by fractionally distilling the 36% acid and collecting the first fraction in a chilled receiver or by condensing hydrogen chloride gas, obtained from a cylinder, in an externally cooled tube. For most samples, ordinary concentrated hydrochloric acid (36%) should be used.

Oxidants. Oxidants which may be used include the following: 70% perchloric acid, 70 and 91% nitric acid, sodium chlorate, chlorine gas from a cylinder, and 30% hydrogen peroxide. All oxidants should be reagent grade.

Perchloric acid is the most convenient oxidant to use if the reaction is to be conducted at temperatures above 250° C. At 250° C or lower it reacts too slowly with hydrochloric acid. Between 250 and 300° C some perchloric acid may remain undecomposed if the heating period is not greater than 24 hr. Nitric acid also is used frequently as the oxidant and is satisfactory throughout the range from 200 to 325° C.

Bursting Pressure of Tubes. An approximate formula for determining the bursting pressure of a cylindrical tube of clear fused-silica or borosilicate glass with rounded ends is

$$P = \frac{2\,WS}{D} \qquad (1)$$

where P = bursting pressure in lb./in.^{2}

W = wall thickness.

D = internal diam.

S = tensile strength in lb./in.^{2} (4,000 for clear fused-silica and 10,000 for borosilicate glass).

In using this formula it must be remembered that the tensile strengths of fused-silica and glass are variable, and defects can cause failure under relatively low pressures. Tubes with heavy walls and a bore of only a few mm. may be expected to withstand high internal pressure, but tubes of the recommended 8-mm. bore and 2-mm. wall thickness have a bursting pressure of about 2,000 lb./in.^{2} for fused silica or 5,000 lb./in.^{2} for glass and require a compensating external pressure.

Pressures Developed by Acid Mixtures at Elevated Temperatures.[1] The pressures developed by 5 ml. of acid solution in an 11.7-ml. space were reported[1] for six systems: 23, 36, and 48 wt. % hydrochloric acid solutions; a mixture of 20 volumes of 36 wt. % hydrochloric acid with one volume of 91 wt. % nitric acid; a mixture of 10 volumes of 36 wt. % hydrochloric acid with one volume of 60 wt. % perchloric acid; and 56 wt. % hydriodic acid. Some of these data are shown in Table I. The data for 23 to 48 wt. % hydrochloric acid in the range 200 to 300° C may be expressed[1] as follows:

Table I

Pressures Developed by Various Acids in a Space of 11.7 Milliliters

Quantities of Acids	Temperature, °C	Pressure, lb./in.^{2}
5 ml. 22.9% HCl	159	125
	191	265
	220	510
	285	1,640
	315	2,550
	338	3,400
5 ml. 36% HCl	178	705
	223	1,430
	285	3,095
	298	3,615
5 ml. 48% HCl	105	525
	166	1,385
	192	1,895
	221	2,490
	253	3,335
	270	3,995
4.76 ml. 36% HCl plus 0.24 ml. 91% HNO_3	106	305
	162	765
	202	1,375
	221	1,670
	236	1,960
	258	2,505
5 ml. 36% HCl plus 0.5 ml. 60% $HClO_4$	101	55
	117	120
	133	205
	163	415
	191	780
	225	1,285
	251	1,985
	284	3,010
	307	3,825
5 ml. 56% HI	160	50
	190	165
	220	320
	254	620
	310	1,570
	327	2,020
	346	2,490

$$\text{Log}_{10}P = (1000/T - 1.345)\,[\tan(0.615\,A + 100.7)] + 4.180 \qquad (2)$$

where P is the pressure in lb./in.^{2} attained at T° K by a solution of A wt. % of hydrochloric acid in a tube which is 43% filled by the acid at room temperature. The angle of which the tangent is to be used in the equation is expressed in degrees.

It is obvious from these data that pressures approaching 4000 lb./in.^{2} are reached during the heating of the sealed tubes, and the bursting pressure of some tubes may be exceeded. Hence, a compensating pressure external to the tube should always be used as a safety precaution. The dimensions of the tubes used in the work described here were somewhat larger than those used to provide the data in Table I. The volume of a 12-in. length of tube having an 8-mm. bore is about 15.3 cc., and, to obtain pressures equal to those given in Table I, the acid volume should be 6.5 ml. For convenience, 7 ml. of acid was used in this work. It is very important to follow the recommendation that the tube, when sealed, should never be more than half-full of solution.

Volume of Free Space in Steel Shell

$$\text{Volume of free space, cc.} = 4.75\,L - 3.14\,R^2H \qquad (3)$$

where L is the internal length of the shell in cm.
R is the external radius of the tube in cm.
H is the length of the sealed tube in cm.

The free space between the steel shell, shown in Fig. 1, and a 12-mm. o.d. tube 30-cm. long is about 140 cc.

Pressure from Carbon Dioxide.[1, 4] In compensating the internal pressure of a sealed tube at elevated temperatures by adding solid carbon dioxide to the steel shell, it is possible to estimate the amount of carbon dioxide which must be used for each cc. of free space and for the maximum temperature that will be reached. Particularly in the range 250 to 300° C, Eq. 4 is applicable:

$$G = \frac{P_c - 750}{53.8\,T} + 0.060 \qquad (4)$$

where P_c = compensating pressure in lb./in.^{2}
T = temperature °C.
G = grams of carbon dioxide to be used for each cc. of free space.

The external pressure on the sealed tube may exceed the internal pressure, especially at some temperatures intermediate between 40° C and the maximum temperature used with the above formula. This difference is not serious because tubes usually are more resistant to crushing loads than to bursting forces. For a free-space volume of 140 cc. and a temperature of 315° C, 35 grams is the calculated quantity of solid carbon dioxide to provide a compensating pressure of about 4000 lb./in.^{2}.

Recommended Conditions for Dissolving Specific Materials. The solvent and oxidant combination most frequently used is 5 to 7 ml. of 36% hydrochloric containing 3 or 4 drops of 70% perchloric acid (Table II). This solvent at 310 to 325° C dissolves 0.2- to 1.0-gram samples of plutonium, ruthenium, and plutonium "fissium" alloys; refractory oxides of plutonium, aluminum, beryllium, tin, cerium, and zirconium-silicon; and 0.2- to 0.5-gram samples of the platinum metals and their alloys. A mixture of 5 to 7 ml. of 36% hydrochloric acid and 3 or 4 drops of 70% nitric acid also may be used for the platinum metals, and some of these, such as iridium and iridium-platinum alloys, are dissolved at 100 to 150° C. With the exception of highly refractory oxides which require heating for periods as long as 40 hr., most samples are dissolved in 2 to 3 hr. For plutonium alloys and other materials that react to some extent with hydrochloric acid at room temperature, the acid is added dropwise to the sample and the initial reaction completed before the quartz tube is sealed. Conditions for dissolving minerals and rocks are described elsewhere.(4)

Table II

Recommended Conditions for Dissolving Specific Materials

Material	Sample wt., grams	Volume HCl, ml.	Oxidant, drops	Temperature, °C
Pu-Ru, Pu fissium, PuO_2, Al_2O_3, BeO, SnO_2, CeO_2, ZrO_2-SiO_2, Ru, Ir, Os, platinum metal alloys	0.2 to 1.0	5 to 7	70% $HClO_4$, 3	310 to 325
Ru, Rh, Ir, Os	0.2 to 0.5	5 to 7	70% HNO_3, 3	310 to 325
Ir-Pt	0.2 to 0.5	5 to 7	70% HNO_3, 3	100 to 150

Recommended Technique for Sealing the Tube. Following addition of sample and solvent, the tubes are chilled in dry ice and sealed off about 3 in. from the open end in the following manner. The tube is held almost upright and rotated in a gas-oxygen flame. As the tube softens, it is repeatedly bent slightly during the rotation, but pulling of the tube is avoided to prevent thinning of the walls. This process is continued until the diameter is quite small; then the tube is pulled slightly and severed by melting with the flame. This technique ensures against small orifices in the seal which might allow carbon dioxide to flow into the tube during the heating, causing a high internal pressure when the tube is removed from the shell. The sealed end is worked down in the flame to a nearly hemispherical shape. This process is hastened by pressing the softened tip against a block of graphite or the tip of the burner to help shape it during the heating. Inadequate chilling of the tube contents or prolonged working of the seal to obtain the correct shape will cause a slight internal pressure which may blow a small bubble or a hole in the soft, sealed end. If this occurs, patch the hole with silica from a small-diameter rod (the thin end of the severed tube tip often suffices), rechill the tube by increasing the amount of dry ice surrounding it, and rework the sealed end to the desired shape. It often is better to accept a seal with a slightly pointed shape than to risk blowing a hole that requires patching.

OPERATION

A fused-silica or borosilicate glass tube of the proper dimensions, depending upon the nature and quantity of sample to be dissolved, is selected. For dissolution of plutonium-containing materials, the sealed end of the tube is inserted into a 16- to 18-millimeter bore glass tube sealed on one end, and the exposed walls of the inner tube and the top of the outer tube are covered and sealed together with masking tape to prevent contamination of these areas with radioactive material. The open end of the inner tube is left unobstructed to admit the sample. For nonradioactive samples, the outer glass tube is not used.

A 0.1- to 1.0-gram portion of the sample is weighed accurately and transferred to the silica or borosilicate glass tube. This operation is performed in a glove box if the sample contains plutonium. The material placed in the tube is either a portion of the entire sample or of the residue remaining following treatment of the sample with hydrochloric acid. Then 7 milliliters of 36 weight percent (12 M) hydrochloric acid are added to the tube. If the sample reacts with the acid, it is added cautiously drop by drop until the reaction ceases. Then the walls of the tube are washed down with the remainder of the 7 milliliters of acid, and 3 or 4 drops of 70 percent perchloric acid are added. (The directions given under Recommended Conditions for Dissolving Specific Materials are followed in determining the quantities and types of acids and oxidants to use.)

After the acids drain from the walls of the tube, it is transferred to a container filled with powdered dry ice. This transfer is easily accomplished for the nonradioactive samples but requires the removal of a plutonium-containing tube from its glass envelope without contaminating the exterior of the tube. This is done by removing the masking tape carefully and then withdrawing the tube from the envelope using an uncontaminated glove or forceps to grasp the tube. The open (contaminated) end is covered with clean masking tape before the tube is placed in the dry ice.

The tube is held behind a safety shield or in an uncontaminated glove box and sealed off at a length of about 12 inches without allowing any thin spots to develop in the heated areas. This seal is allowed to cool to room temperature. If a temperature of 200° C or higher is used in the dissolution, or the material being dissolved contains plutonium, the tube is enclosed in a steel shell. To calculate the quantity of carbon dioxide to provide a compensating pressure, the free space between the shell and the sealed tube first is calculated. Then the internal pressure in the sealed tube, at the temperature and for the concentration of acid to be used, is estimated from the data given in Table I. Using these data and Equation 4, the weight of carbon dioxide required is calculated. For a tube 30-centimeters long, 8 millimeters in bore diameter, and containing 6 to 7 milliliters of 36 weight percent hydrochloric acid, approximately 35 grams of dry ice are added to the steel shell to create the desired compensating pressure if the sample is to be heated to 310 to 325° C. Tubes heated to less than 200° C are held in a length of 1/2-inch pipe closed with threaded pipe caps unless the sample contains radioactive material.

The threads and gasket surfaces of the steel shell are coated with Aquadag, and the sealed tube is inserted. The calculated quantity of solid carbon dioxide is added, the cap is quickly screwed onto the shell to seal it, and the shell is placed under water to test for leaks. When properly sealed, the shell is tipped back and forth to distribute the sample along the length of the tube and then placed horizontally in an oven heated to the desired temperature.

Following the estimated time required to dissolve the sample, the steel shell is removed from the oven and allowed to cool to room temperature (usually 2 hours). Then the cap is loosened to allow the carbon dioxide to escape slowly. This operation is done in a glove box if the sample is radioactive, and the off-gas is monitored for alpha contamination to

determine if the glass or silica tube has broken. If the gas is radioactive, the shell is quickly resealed and discarded according to standard operating procedures for disposal of contaminated wastes. If the gas is not radioactive, the steel nut is removed from the shell in a glove box or behind a safety shield while the gas pressure is expended. Heavy rubber or leather gloves are worn while the open end of the plastic tube (see Fig. 2) is inserted into the shell and pressed firmly into the metal cup in the bottom of the shell. The plastic tube with the glass or silica tube supported inside by the metal cup is removed, and the sample is inspected to determine if dissolution is complete. If the sample is not completely dissolved, the tube is replaced in the shell, the calculated weight of solid carbon dioxide added, and the shell sealed and heated as described previously. When visual inspection shows that the sample is dissolved, the metal cup is removed from the end of the plastic tube, and the silica or glass tube is slid carefully into a Dewar flask containing sufficient liquid nitrogen to cover the portion of the tube that contains solution. The solution is allowed to freeze solid, and the silica tube is removed from the liquid nitrogen and carried in the transfer unit to either a contaminated glove box, (for plutonium-containing samples) or behind a safety shield (for nonradioactive samples) where the tube is scored with a file and broken open. Heavy rubber gloves or leather gloves are worn while opening the tube. The ends of the tube are inverted in a beaker containing a few milliliters of water, and the solution is allowed to melt and flow into the water. The remaining solution is washed quantitatively from the tube with water.

APPLICATIONS

In our Laboratory this dissolution method was first applied, more than 20 years ago, to the dissolution of refractory oxides, such as high-fired magnesia, and beryllia that were being analyzed for low concentrations of boron. Prolonged refluxing with acids or fusion with acidic or basic

fluxes were avoided because of possible loss of volatile boric acid or contamination of the sample with boron. From 100 to 500 milligrams of the refractory oxide and the measured quantities of 36 percent hydrochloric acid were sealed in fused-silica tubes which were enclosed in iron pipes and heated to 200° C overnight (about 16 hours). The same general method was applied to the dissolution of the noble metals, such as iridium, rhodium, osmium, and ruthenium, and also some binary alloys of the noble metals. The solvent for these metals was 36 percent hydrochloric acid containing 3 or 4 drops of 70 percent nitric acid. Either borosilicate glass or fused-silica tubes were satisfactory for the dissolution of the platinum metals, but fused-silica tubes were necessary for dissolving the materials to be analyzed for boron.

Approximately 10 years ago facilities were obtained for applying the sealed-tube method to refractory plutonium materials, and one of the first of these was partially fused (2200° C) plutonia. The sample, 7 milliliters of 36 percent hydrochloric acid, and 4 drops of perchloric acid were sealed in fused-silica tubes and heated to 310° C. Approximately 50 hours were required to dissolve 0.3 to 0.5 gram of this refractory oxide (Table III). This long and drastic treatment also dissolved some of the silica from the tube. The silica was in the form of a fine white powder when the tube had cooled. Spectrochemical analysis showed that this powder, which was soluble in hydrofluoric acid, was mainly silica contaminated with traces of plutonium. This attack of the silica tube was not extensive enough to weaken the tube significantly, but the visible quantity of silica powder adequately emphasized the fact that the sample had been contaminated with material from the tube.

The applications of the method that have been made in this Laboratory and the dissolution conditions are summarized in Table III. These applications were made successfully and without difficulties. However, the dissolution of plutonium "fissium" alloys showed the need to select

Table III

Materials Dissolved in Hydrochloric Acid[a] by the Sealed Tube Method

Material	Quantity, grams	Type Tube	Oxidant[b]	Temperature, °C	Dissolution Time, hr
Pu fissium[c]	1 to 2	silica	$HClO_4$	310[d]	2 to 3
PuO_2(sintered)	0.2 to 0.5	silica	$HClO_4$	310	50 to 100
PuO_2 (700 to 1200° C)	0.2 to 0.5	silica	$HClO_4$	310	2 to 4
PuO_2 + Re	0.1 to 0.3	silica	$HClO_4$	310	4 to 6
PuO_2 + W (sintered)	0.2 to 0.8	silica	$HClO_4$	310	8 to 10
PuO_2+ Mo (sintered)	0.2 to 0.8	silica	$HClO_4$	310	8 to 10
Re	0.1 to 0.3	silica or glass	$HClO_4$	310	4 to 16[e]
Ir, Rh, Ru, Pt	0.1 to 0.3	silica or glass	HNO_3	310	2 to 16[e]
Ir, Rh, Ru, Os	0.1 to 0.3	silica or glass	HNO_3	200	16[e]
Re-W-Mo alloy	0.2 to 0.5	glass	$HClO_4$	310	16[e]
Rh-Ir alloy	0.1 to 0.3	silica or glass	HNO_3	200	24 to 48
Rh-Ir, Rh-Pt, Pt-Ir, Pt-Ru, Pd-Rh, Pd-Ru, Pd-Ir; Pt-Pd	0.1 to 0.3	silica	$HClO_4$	310	16[e]
ThO_2 (high-fired)	0.1 to 0.3	silica	$HClO_4$	310	3 to 16[e]
MgO	0.1 to 0.5	silica		200	16[e]

[a]Thirty six wt. % HCl, 7 ml.

[b]Three to four drops of oxidant used.

[c]Pu, 92%; Fe, 2.8%; Ce, 0.74%; La, 1.31%; Mo, 0.74%; Nb, 0.03%, Ru, 1.28%; Zr, 0.82%.[3]

[d]Tubes heated above 200° C are enclosed in a steel shell.

[e]Overnight in furnace; this convenient time probably is greater than the minimum time required in some cases.

the solvents carefully for each material. In this case about 90 percent of the sample dissolved when hydrochloric acid was added, and the main need for the sealed tube method was to dissolve the residue without loss of ruthenium. However, a small quantity of white powder, determined by chemical analysis to contain mainly zirconium, occasionally was found in the sealed tube following the 2-hour heating period. This powder was not dissolved by further heating. The occurrence of the zirconium-containing residue was subsequently correlated with the use of hydrochloric acid less concentrated than 36 percent that had been taken from frequently opened reagent bottles. Fresh 36 percent hydrochloric acid completely dissolved the fissium alloy, and 45 percent hydrochloric acid probably would prove to be a more reliable solvent for zirconium-containing materials.

In the hands of properly trained and careful analysts, repeated use of this method has shown it to be safe, reliable, and in many cases less time-consuming than other dissolution techniques. With the exception of slight contamination of the sample with material dissolved from the tube, mainly silica, a "clean" hydrochloric acid solution, free of large quantities of added salts, is obtained. The possibilities of losing volatile constituents from the sample are minimized also. The method is applicable to highly radioactive materials without undue danger of contaminating the laboratory provided adequate precautions are taken and suitable facilities are used.

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