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A RAPID DECOMPOSITION METHOD FOR ANALYZING ZIRCONIA

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ABSTRACT.— A rapid method is presented for the decomposition of zirconia using a suitable combination of (NH4) F + $(NH_4)_2SO_4$ as fusion agent at about 350°C. The cooled melt (cake) is easily soluble in acidified water in 15-20 minutes. The sample solution may be used for recovery of many components using several analytical methods. During the composition silica is volatilized completely.

INTRODUCTION

Due to its particular physical and chemical properties (e.g. high melting point and resistance to acids and alkalis) the element zirconium and also its compounds have a wide variety of applications in industrial and nuclear technology. The oxide of zirconium (zirconia) is one of the main component of glazed enamels and is largely used for opacity of ceramics as well as in ceramic color technology. Furthermore, zirconia is commonly used in manufacture of alkali resistant ceramics and is one of the fundamental components of refractory materials, briquetts etc.

Technical applications of zirconium compounds are extensive in the electronic and electrotechnical industries. Zirconium is also used in high vacuum technology, catalyst techniques, in the pharmaceutical industry as well as in the manufacturing of special glasses and synthetic gems (Gmelin, 1958; Hathaway, 1984).

In nature zirconium mainly occurs as silicate (e.g. zircon) and oxide (e.g. baddeleyite) which are commonly associated with magnetite ilmenite, monazite, rutile, garnet, sillimanite, quartz etc.

Of the twenty seven commonly known zirconium-bearing minerals which contain variable amounts of actinides and rare earth elements (Vlasov,1966),zircon and baddeleyite are the most interesting for science and technology.

The mineral zircon is not only for interest because of its zirconium concentration, but also because of its application in geochronological studies, whereas baddeleyite is commonly used in industrial purposes.

In the concentration of zirconium and manufacture of zirconia several methods (e.g. magnetic—, wet-mechanical separations, floatation technique)are used. These procedures do not seek to obtain absolutely pure zirconium concentrates. It is, however, necessary to know the amount of impurities (e.g. silica, alkali, aluminium, titanium, iron, manganese) before it may be used for industrial applications.

The determination of zirconium concentration in the dissolved samples may be performed easily by the usual analytical methods (e.g. by titrimetric-, gravimetric-, or spectrometric-methods). However, not only the determination of impurities from the same sample solution may involve difficulties in analysis (due to the higher zirconium concentration in the matrix) but also because the complete decomposition of zirconium minerals is difficult to ensure.

This paper deals with the disintegration problem of zirconia and represents a part of the paper "A Rapid Decomposition Method for Analyzing Zirconium Minerals and Zirconia" read in 8. Spectrometer Meeting, Baden - Baden FRG. 1986.

ANALYTICAL PROCEDURES

The decomposition technique commonly used to dissolve zirconia depends on the composition of minerals and also the preliminary thermal treatment. The disintegration of samples can be carried out by acid attack as well as by fusion methods.

Acid attack method

The disintegration of samples may be performed by reaction with conc. H_2SO_4, H_2SO_4+HF, HNO_3+HF. In order to dissolve one of the highly resistant zirconium materials, zirkite (consisting of a mixed fibrous baddeleyite, zircon, altered zircon (orwillite), and other minerals) requires four times the sample weight of conc. H_2SO_4 with a decomposition time of 2 h at about 400°C. On the other hand, the mineral cyrtholite is attacked using two times the sample weight of excess conc. H_2SO_4 at about 210-220°C for 30 minutes (Gmelin, 1958). A H_2SO_4 acid attack on zirconium material produces water soluble zirconium sulphates.

HF is also one of the efficient disintegration agents used for the decomposition of zirconium minerals and acts by converting zirconium to a soluble zirconium fluoride (1.388 g/100 ml). However, due to its low boiling point (max. 112°C) HF is rather inefficient during open vessel acid attack procedures. Instead of HF, an efficient acid attack can be performed using CaF_2 (m.p. 1360°C) with conc. H_2SO_4 (max. boiling temperature of conc. acid d 339°C). If the decomposition is carried out by $CaF_2+H_2SO_4$ (using 2 parts of CaF_2+2.5 parts of conc. H_2SO_4) either $H_2[ZrF_6]$ + $CaSO_4$ or basic zirconium-sulphate is formed (Weiss, L.; Marden, J.W. and M.Rich, in Gmelin, 1958). This procedure causes the loss of silica as SiF_4, and a part of titanium as TiF_4.

The common acid attack disintegration of zirconia at high temperature in a platinium vessel is not a suitable procedure because of the volatilisation and splashing of acids before the sample is completely dissolved. Due to incomplete decomposition of zirconia, the procedure is better performed in an autoclave using HF+H_2SO_4, HF+HNO_3 as used for zircon (Ito, 1962; Krough, 1973).

One of the very promising acid attack procedures used for the analysis of zirconia and titania is presented by Bastius (1984): Zirconia and titania are attacked by HF+H_2SO_4 in presence of ammonia. The more resistant materials are decomposed with an acid attack of H_2SO_4+.$(NH_4)_2SO_4$, so that the boiling point of H_2SO_4 is elevated. Furthermore, Bastius uses a two-step treatment: The highly resistant samples are attacked initially by $H_2SO_4+(NH_4)_2SO_4$ and then these are decomposed by HF+(NH_4)F. Possible contamination, which may occur using $(NH_4)_2SO_4$ is minimized by using high quality NH_3, H_2SO_4, HF.

Fusion method

Fusion methods commonly used for zirconium material analysis are carried out with a variety of fluxes, such as NaOH, Na_2O, Na_2O+NaOH, Na_2O+ Na_2CO_3, NaF+$Na_2B_4O_7$, $NaHSO_4$, KF, KHF_2, $NaHF_2$ (Bock, 1979, Dolezal, et al., 1968; Gmelin, 1958).

The cooled melt is dissolved by selected acids. These fusion procedures of zirconia mentioned above have several disadvantages due to the various fluxes used, which yield undesirable components (overloading) in the solution of sample. In addition, if the sample decomposition is carried out at low temperatures, the sample may not be dissolved completely, whereas at temperatures that are too high insoluble zirconium compounds (e.g zirconium—oxide) are produced.

The ammonium salts (e.g. (NH_4)F, $(NH_4)_2SO_4$, (NH_4)C1) have also been used as fusion agents to decompose ores and silicates (Bock, 1979; Dolezal, et al., 1968, Liteanu and Paniti, 1972, Milner, et al., 1967; Verbeek, et al., 1970).

Shead and Smith (1931) performed ammonium fluoride fusion for the decomposition of refractory silicates (e.g. sillimanite), and the analysis of silica from glass sand.

Bayer, et al. (1982) reported sulphate reaction of Si—, Al—, Fe—, Mg—, Ti—bearing silicate minerals, where reactions were carried out with ammonium sulphates at 350—550°C. Due to the particular affinity of zirconium for ammonia slightly soluble, double ammonium—zirconium sulphate compounds may be produced during the disintegration of zirconium material by H_2SO_4 in presence of ammonia.

Devillebichot (1983) decomposed zirconia by ammoniumbifluoride for the producing of ammoniumheptafluorozirconate. If NH_4HF_2 (m.p. 125°C) is used to attack zirconia complete decomposition of sample can not be obtained. This is due to the lower boiling temperature of the flux and is also dependence on the preliminary thermal treatment of starting material. After adding $(NH_4)_2SO_4$ m.p.235°C to the NH_4HF_2, the melting point of ammonium bifluoride can be elevated, this aims to additionally minimalize the volatilisation of zirconium and titanium as fluorides and the formation of all zirconium as zirconium-fluorides. The use of $(NH_4)_2SO_4$ as fusion agent for the decomposition of zirconia is connected with some difficulties, due to the impurities of silicates, which may be present in the sample and do not react during the disintegration procedures.

The addition of a complementary compound such as NH_4HF_2 (or NH_4F) to the $(NH_4)_2SO_4$ produces a potential flux, which is more efficient than alone using $(NH_4)_2SO_4$ or NH_4HF_2 in disintegration procedures of zirconia as fusion agent.

Decomposition of zirconia using $(NH_4)_2SO_4$+ $(NH_4)F$ as a fusion agent can be carried out also for the production of slightly soluble double—sulphates and fluorides of Zr, Ti, Fe, Al. During the disintegration the silica is volatilized completely. This procedure may be considered similar to an acid attack carried out by H_2SO_4+HF at 350°C, but it is less dangerous and more effective than the H_2SO_4+HF disintegration.

RAPID DISINTEGRATION PROCEDURE

A rapid decomposition of zirconium material may be obtained if the material is fused with a suitable combination of $(NH_4)F+(NH_4)_2SO_4$. This method is preferred because of its convenience compared to acid attack and the use of fluxes because of potential excess components being included. The fusion of zirconia is performed by $(NH_4)F+(NH_4)_2SO_4$ in a 25 ml covered platinum crucible using a tubular furnace.

Tubular furnace

This is made using a ceramic tube which is closed at one end and is 300—350 mm in lengh and about 100 mm in diameter. The heating is performed by a heating band, which should be well isolated to prevent temperature gradients. The oven is heated to 350°C and the temperature is measured by an inserted thermoelement (or thermometer). An outlet is needed for the escape of fumes that evolve during the decomposition of the sample.

Sample decomposition

The experimental procedure presented in this paper, was carried out on a 1000 mg sample (zirconia) which was mixed with 2500 mg $(NH_4)F$+5000 mg $(NH_4)_2SO_4$ in a closed platinum crucible and disintegrate for 45-60 minutes at 350°C.

At about 350°C the sample (with flux) is placed in the tubular oven and left for 45—60 minutes for the fusion procedure. The crucible is quenched after removal from the oven and transferred to a beaker containing 50—100 ml cold water + 1—1.5 ml conc. HC1 (37%). Instead of HC1, H_2SO_4 may also be used. Heating of the solvent which is used to dissolve the cooled melt (fusion cake) is not necessary and it should be avoided to prevent the formation of insoluble zirconium compounds. The cake is dissolved very quickly (during 15—20 minutes) by stirring using a magnetic-bar and stirrer. After dissolving the cake in acidified water a clear solution is obtained. Experience shows that for the decomposition of samples with a high content of silica (e.g. 15 %) the relative amount of $(NH_4)F$ must be increased up to 5000 mg. In a forthcoming paper the application of this flux combination, to analyse silicate rock samples will be discussed in detail (Ayrancı, in prep.).

The reproducibility of this procedure is checked by applying it simultaneously to three aliquots of a sample. It was found that the samples gave the same results within the analytical error, which itself depends on the method being used. The components of the sample solutions were analyzed by AAS and ICP. The analytical results of this experimental work and the recovery of individual element concentrations will follow.

Table 1

	Al		Fe		Ca		Ti		Remarks
	Cert.	Recov.*	Cert.	Recov.**	Cert.	Recov.*	Cert.	Recov.*	
Aliquot 1	<500	470	<40	45	<15	25	<15	12	Recovered values are mean of AAS and ICP analyses
Aliquot 2	<500	460	<40	55	<15	20	<15	18	
Aliquot 3	<500	490	<40	50	<15	20	<15	17	

Starting Material: Zirconia, U.P.H. (grain size 0.04-0.5 m., contains 2.5 % HF), Cricerom, France.
Certified impurities: Al < 500, Ca < 15, Fe <40, Mg <2, Na < 15, Si <30, Ti <15 ppm.3 Aliquots of zirconia simultaneously decomposed with (NH.) F + $(NH)_2SO_4$ in closed platinum crucibles at about 350° C for 55 minutes. Aliquot 1.2.3: 1000 mg zirconia + 2500 mg (NH_4) F + 5000 mg $(NH_4)_2SO_4$ After dissolving cooled melt in an acidified water (containing 1.5 ml conc. H_2SO_4 in 100 ml H2O), the given elements were analized.

* Measured by AAS and ICE
** Recovered by AAS and Spectrometric procedures.

CONCLUSIONS

The disintegration of zirconium materials using $(NH_4)F+(NH_4)_2SO_4$ as a fusion agent and dissolving the cooled melt (fusion cake) by dilute acids (e.g. HC1, H_2SO_4) yields negligible concentration of extra components that are undesirable for the recovery of components in analytical procedures. Due to the absence of several components (e.g. KF, NaOH, $Na_2B_4O_7$, CaF_2, Na_2O) it is also possible to analyse these components themselves in the sample solution.

The sample disintegration by $(NH_4)F+(NH_4)_2SO_4$ in a closed platinium crucible is rapid and it is also less dangerous than a common H_2SO_4+HF acid attack carried out in open vessels. After the disintegration of sample using such ammonium fluxes, mostly double ammonium sulphates of the elements Al, Ti, Fe, Zr and (perhaps) also ammonium zirconium fluorides are formed. These products are slight soluble in acidified water. The sample disintegration is completed quickly and at low temperatures (about 350°C).

During the fusion of zirconium minerals using $(NH_4)F+(NH_4)_2SO_4$ silica is completely volatilized as SiF_4, H_2SiF_6. The mothod may be used for the routine analysis of zirconia in samples of various weights, and in runs of various sample.

The known chemical affinity of zirconium for ammonium in presence of H_2SO_4 to produce water-soluble double ammonium—zirconium sulphates and ammonium zirconium fluoride may be utilized if the zirconium material is decomposed by $(NH_4)F$ + $(NH_4)_2SO_4$ or $(NH_4)HF_2+(NH_4)HSO_4$ in a closed platinium crucible. This procedure is similar to a H_2SO_4+HF acid attack method, which is well known in "rapid silicate analysis" to prepare a "solution B" (Maxwell, 1968). The procedure may also be used for the disintegration of silicate rocks and minerals as an alternative decomposition method.

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