

DETERMINATION OF GALLIUM IN ALUMINIUM COMPOUNDS BY ATOMIC ABSORPTION SPECTROMETRY

Věnceslava TOKAROVÁ and Josef MAREČEK

Chemopetrol, Research Institute of Inorganic Chemistry, 400 60 Ústí nad Labem

Received April 27th, 1987

A method is suggested for the determination of gallium in aluminium oxide and in raw materials for its production (aluminium sulphates, alums) by atomic absorption spectrometry with electrothermal atomization, based on direct injection of a suspension of Al_2O_3 in an ethanol-water 9 : 1 mixture into a tungsten atomizer. Suspensions of Al_2O_3 with known amounts of Ga embedded in the solid phase are found to suit best for calibration. Optimum heat treatment and atomization conditions are established. The behaviour of gallium in aqueous solutions and in Al_2O_3 suspensions during their heat treatment is compared for atomization in a tungsten atomizer and in a graphite furnace.

Analysis of trace impurities in Al_2O_3 and in raw materials for its production is gaining in importance as high-purity $\alpha\text{-Al}_2\text{O}_3$ is being increasingly used for the manufacture of transparent ceramics. Among elements followed is gallium which accompanies natural aluminium materials owing to its close relation to this element. For the above manufacturing purposes, gallium in Al_2O_3 has to be determined at levels as low as unit ppm.

The determination of 0.2–2% Ga in aluminium compounds has been the concern of Egorova and coworkers¹, who devised a titrimetric procedure in acetate solutions (pH 5) using disodium ethylenediaminetetraacetic acid as titrant and xylenol orange as indicator. The determination of this element in technical aluminium and its alloys by AAS in a flame (for mass fractions $w_{\text{Ga}} > 2 \cdot 10^{-4}$) and in a graphite furnace (for $w_{\text{Ga}} < 2 \cdot 10^{-4}$) has been studied by Gorlova and Veller². The depressive effect of aluminium on the determination of gallium in the electrothermal atomization mode has been discussed and the use of solutions containing aluminium in concentrations not exceeding 0.5 mg ml^{-1} advised; at this concentration the signal of gallium is one-half relative to that for a solution free of aluminium. If a solution with a higher aluminium concentration is used, a constant signal is obtained, which the authors fail to offer an explanation for. The method suggested enables gallium in aluminium materials to be determined at a level of tens ppm. Nonselective absorption is eliminated by correction using a deuterium lamp.

Sukhoveeva and coworkers³ used AAS-ETA with a graphite furnace fitted with a platform, and compared the effect of various matrices such as HCl, HNO_3 or

extracts in organic solvents; they did not concern themselves, however, with the analysis of aluminium-containing materials. Anderson and coworkers⁴ determined gallium in rocks by AAS-ETA after separation by ion exchange chromatography. Again, the matrices were not ones with dominating aluminium. The determination of gallium in sediments, light ashes and plants in a graphite furnace using nickel as a matrix modifier has been described by Chinese authors⁵. Addition of nickel nitrate to a solution of gallium in nitric acid (0.1 mol l^{-1}) brought about a sixfold signal increase and allowed the combustion temperature to be increased from 900°C to 1200°C . This favourable effect of nickel has been explained in terms of the formation of thermostable compounds with gallium, whereupon combustion losses are reduced.

In the present work, a method for the determination of gallium in Al_2O_3 based on direct injection of Al_2O_3 suspension into a tungsten atomizer is suggested. A similar approach has been used by Slovák and Dočekal⁶ for the determination of some other elements such as chromium and lead in Al_2O_3 using a graphite furnace. Its advantage lies primarily in the fact that high-pressure sample decomposition can be thus omitted; calibration, however, is a problem because atomization of gallium embedded in particles of Al_2O_3 will be probably somewhat different from that with gallium on the particle surface. Hence, it can be expected that the slope of a calibration plot obtained by using solutions prepared by adding a standard solution of gallium to a liquid suspension of pure Al_2O_3 will be different from that of a calibration plot for a suspension of Al_2O_3 with gallium incorporated in the solid particle. A comparison of the two approaches is the objective of this work. Attention is also paid to the optimization of conditions of measurement on standard aqueous gallium solutions, particularly the temperature, time and heating rate in the heat treatment (combustion) and atomization processes. The signals of gallium in standard solutions and in Al_2O_3 obtained using a graphite furnace and a tungsten atomizer are also compared.

EXPERIMENTAL

Apparatus

The AAS measurements were carried out on a Varian AA-775 ABQ instrument at $\lambda = 294.4 \text{ nm}$, slit width 0.5 nm , hollow cathode lamp current 7 mA . Nonselective absorption was eliminated by correction using a deuterium lamp.

Atomization was achieved in a CRA-90 graphite furnace (Varian Techtron, Victoria, Australia) or in a WETA-82 tungsten atomizer (Laboratorní přístroje, Prague). The graphite furnace was cooled with water and screened with argon at a flow rate of 4 l min^{-1} . Sample was dried for 40 s at 90°C , combustion was carried out for 20 s at various temperatures. Atomization was accomplished at 1800°C for 2 s using a temperature increase rate of 700 K s^{-1} . Suspensions of Al_2O_3 with Ga were injected into the preheated furnace, combustion temperature was 800°C .

The tungsten atomizer was cooled with water and flushed with argon and hydrogen at flow rates of 2 and 0.2 l min⁻¹, respectively. Sample was dried in two steps, viz. at 90°C for 25 s and then at 120°C for 15 s. Other conditions were variable.

Standard Samples

Aqueous solutions for measurements with a graphite furnace. Solutions in HCl (0.2 mol l⁻¹) were prepared in gallium concentrations of 0.1 and 0.4 µg ml⁻¹. In order to prevent evaporation of gallium in the chloride form, similar solutions containing, in addition, ammonium nitrate in a final concentration of 0.2 mol l⁻¹ were also used. The volume injected was 5 µl, which corresponded to 0.5 and 2 ng Ga.

Aqueous solutions for measurements with a tungsten atomizer. A stock solution containing gallium in a concentration of 10 µg ml⁻¹ in H₂SO₄ (0.05 mol l⁻¹) was prepared and diluted as required. Volume injected was 5 µl.

Suspensions of Al₂O₃ containing gallium in the solid phase. 0.5 g of Al₂O₃ of 99.999% purity (Ventron, F.R.G.) was decomposed for 3 h at 160°C in stirred 10 ml of H₂SO₄ (1 : 1) of Suprapur grade (Merck, F.R.G.) in an autoclave fitted with a Teflon insert (Perkin-Elmer, F.R.G.). The solution was transferred to a 50 ml volumetric flask and diluted to volume with water. Three 10 ml aliquots of this solution were pipetted into platinum crucibles; the first was left intact, to the second and third was pipetted a solution contributing 1 and 2 µg Ga, respectively. The solutions were evaporated to dryness and the residue was calcinated for 1 h at 900°C. After cooling, the Al₂O₃ prepared was ground in a corundum mortar. In this manner, standard samples of Al₂O₃ containing 0, 1 · 10⁻³, and 2 · 10⁻³% Ga, respectively, were obtained. Samples with higher gallium contents were prepared likewise.

50 mg portions of these Al₂O₃ samples were placed in 25 ml beakers and 5 ml volumes of an ethanol-water 9 : 1 mixture were added, and the whole was stirred with an electromagnetic stirrer. The suspensions contained aluminium oxide in a concentration of 10 mg ml⁻¹, hence, gallium in concentrations of 0, 0.1, and 0.2 µg ml⁻¹, respectively. In case that higher gallium concentrations were to be determined, standard aluminium oxide samples doped with higher quantities of gallium were used and suspensions containing Al₂O₃ in amounts lower than 10 mg · ml⁻¹ were prepared. The concentrations of gallium measured lay within the regions of approximately 0–0.2 µg ml⁻¹. For the analysis, the concentrations of Al₂O₃ in the calibration suspension and in the sample suspensions were at the same levels.

Suspensions of Al₂O₃ containing gallium in the liquid phase. To 50 mg portions of fine pure Al₂O₃ in three beakers were added 0, 0.5, and 1 µg Ga, respectively, and the systems were diluted to 5 ml with an ethanol-water 9 : 1 mixture. In this manner, suspensions containing Al₂O₃ in a concentration of 10 mg ml⁻¹ and Ga in concentrations of 0, 0.1, and 0.2 µg ml⁻¹, respectively, were obtained. Stirred suspension sample was taken and injected into the atomizer similarly as above.

The calibration plots obtained with the aqueous standard solutions and suspensions prepared by the two procedures are shown in Fig. 1.

Conditions for the Determination of Gallium in Al₂O₃

Gallium in Al₂O₃ was determined using suspensions with known amounts of gallium incorporated in the solid phase for calibration. Finely ground sample was worked up as above to obtain a suspension, which was injected into the tungsten atomizer. The following conditions were adjusted: drying (see above), combustion at 250°C for 10 s and at 400°C for additional 20 s,

atomization at 2400°C for 2 s. For Ga concentrations lower than $2 \cdot 10^{-3}\%$, suspension with Al_2O_3 concentration of 10 mg ml^{-1} and Ga concentration between 0 and $0.2 \mu\text{g ml}^{-1}$ was used. The calibration plot was constructed in terms of peak heights. Single-point calibration is feasible where not very high demands are placed on the accuracy.

Determination of Gallium in Aluminium Sulphate and Ammonium Aluminium Sulphate

Sample (3 g) was calcinated in a platinum dish at 900°C for 1 h, ground and worked up to obtain a suspension in which gallium was determined as above.

The use of the standard addition method is also feasible. In this approach, solutions free from or containing an addition of gallium are evaporated in platinum dishes, calcinated to Al_2O_3 and worked up to obtain suspensions for injection. The signal of sample with an addition of gallium should be approximately twice as high as that of sample free from it, and both should lie within the linearity range of the calibration plot.

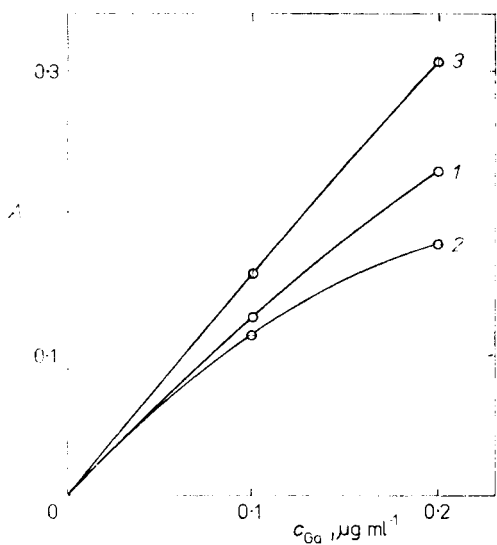


FIG. 1

Calibration plots for the determination of gallium with Al_2O_3 using a tungsten atomizer. Injected volume $5 \mu\text{l}$, atomization temperature 2400°C , time 2 s, heating rate 5000 K s^{-1} . Suspensions contained Al_2O_3 in a concentration of 10 mg ml^{-1} in ethanol-water 9:1 mixture. 1 Standard aqueous solutions of $\text{Ga}_2(\text{SO}_4)_3$, 2 suspensions of high-purity Al_2O_3 containing Ga in the liquid phase, 3 suspensions of Al_2O_3 with defined quantities of Ga embedded in the matrix

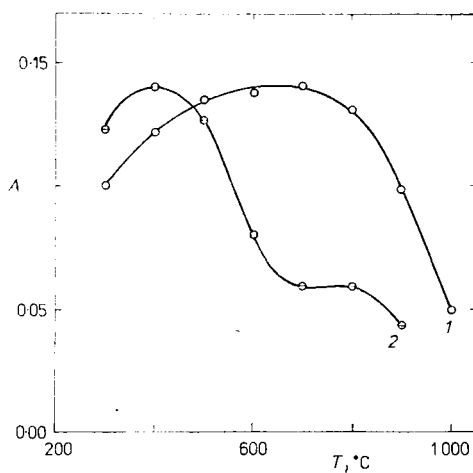


FIG. 2

Dependence of signal of 0.5 ng Ga on combustion temperature. 1 Graphite atomizer, atomization temperature 1800°C , time 2 s, heating rate 700 K s^{-1} , gallium in HCl (0.2 mol l^{-1}) in the presence of NH_4NO_3 (0.2 mol l^{-1}); 2 tungsten atomizer, atomization temperature 2400°C , time 2 s, heating rate 5000 K s^{-1} , gallium in the sulphate form

RESULTS AND DISCUSSION

Behaviour of Gallium During Combustion in Graphite Furnace

The dependence of the signal of gallium on temperature is shown in Fig. 2. Curve 1 demonstrates that evaporation of gallium trichloride, with a boiling temperature of 201.3°C (ref.⁷), appears even at the lowest combustion temperature, viz. 300°C. During the combustion, a fraction of gallium trichloride probably evaporates (unless ammonium nitrate is present) and a fraction is reduced to the metal owing to the intimate contact of sample with the graphite furnace wall. The vapour tension of gallium metal⁷ (Table I) manifests itself at temperatures in excess of 800°C.

Behaviour of Gallium During Combustion in Tungsten Atomizer

The tungsten atomizer must be operated using a protective argon-hydrogen atmosphere to prevent oxidation of the atomizer material. Hydrogen is a reductive medium and takes a significant part in the chemical processes during the combustion. The measurements were performed with a standard solution of gallium(III) sulphate containing Ga in a concentration of 0.1 µg ml⁻¹, where evaporation of chloride is impossible.

Curve 2 in Fig. 1 demonstrates that the behaviour in the tungsten atomizer is different from that in the graphite furnace. Although the protective atmosphere containing approximately 10% (v/v) hydrogen forms a reductive medium, its role is less marked than that of the intimate contact of sample with graphite. Gallium(III) sulphate is probably converted to gallium(III) oxide and partly reduced to gallium(I) oxide which evaporates from the atomizer even at 400°C (it sublimes⁷ at 500°C) and perhaps also to gallium metal. The signal of gallium is additionally lowered if the temperature is raised to above 800°C, probably due to evaporation of gallium.

TABLE I
Gallium vapour pressure at various temperatures⁷

<i>t</i> °C	<i>P</i> mPa	<i>V</i> ^a ml
700	0.0868	668
800	2.75	23.2
900	48.3	1.45
1 000	541	0.14

^a Volume of inert gas requisite for evaporation of 0.5 ng Ga during equilibrium saturation.

It is therefore advised not to increase the combustion temperature to above 400°C when using the WETA-82 device.

Atomization of Gallium in Tungsten Atomizer

Measurements with standard aqueous solutions of gallium(III) sulphate revealed that the optimum atomization temperature is 2 200°C; the determination, however, has to be accomplished at 2 400°C for the Al_2O_3 to be completely removed. The atomization time was 2 s. The high thermal conductivity of tungsten allowed us to adjust the temperature increase rate at $5\,000\text{ K s}^{-1}$ at which the sensitivity was highest ($A = 0.110$ for 0.5 ng Ga); at higher heating rates the reproducibility of determination grew appreciably poorer.

Determination of Gallium in Al_2O_3 in Graphite Furnace

Double atomization peaks were obtained, which indicated that the atomization proceeded in two steps, first from the surface and then from the particle bulk. This might be probably eliminated by using higher heating rates, which, however, was impracticable with the graphite furnace employed. Double peaks had been also observed before during the determination of aluminium in brine.

Determination of Gallium in Al_2O_3 in Tungsten Atomizer

Calibration was the crucial problem for the determination of Ga in Al_2O_3 . Fig. 1 demonstrates that high differences exist between the calibration plots for aqueous solutions, suspensions of Al_2O_3 containing gallium in the aqueous phase and suspensions of Al_2O_3 with gallium embedded in the solid matrix, and that the last approach is correct; in this manner, gallium can be determined in Al_2O_3 in concentrations as low as $2 \cdot 10^{-4}\%$ with a relative error of about 15–20%.

Determination of Gallium in Aluminium and Ammonium Aluminium Sulphates in Tungsten Atomizer

If directly delivered, aluminium (in concentrations about 5 mg ml^{-1}) in the sulphate caused too high depressions, due to which the sensitivity of determination dropped appreciably. Therefore, samples were calcinated and the oxides were subjected to analysis in suspensions. The determination of gallium in the sulphates by the standard addition method was compared to that using calibration with standard Al_2O_3 suspensions; the error observed lay within the limits of error of determination. Hence, modelling the matrix with high-purity Al_2O_3 is satisfactory, the minority components in sample causing no appreciable interferences.

The levels of gallium found in various aluminium compounds were as follows (in %): aluminium sulphate cryst., techn. (Lučební závody, Kolín) $3.8 \cdot 10^{-3}$, am-

monium aluminium sulphate (U.S.S.R.) $3.3 \cdot 10^{-4}$, aluminium hydrate, 65% Al_2O_3 (Závod SNP, Žiar nad Hronom) $3.1 \cdot 10^{-3}$, aluminium oxide (Ceraver, France) $2.2 \cdot 10^{-3}$, aluminium oxide from recrystallized aluminium sulphate $5.0 \cdot 10^{-4}$.

In conclusion, the tungsten atomizer is superior to the graphite furnace in the possibility of using considerably higher heating rates owing to the high thermal conductivity of tungsten and low thermal capacity of the atomizer. A shortcoming of the tungsten atomizer is in the fact that the combustion temperature has to be held below 400°C (as against the 700°C for the graphite furnace), but this is not a serious drawback in view of the fact that Al_2O_3 cannot be removed completely anyway at either of the two temperatures. The injection of the suspension into the atomizer is convenient, the decomposition of sample in an autoclave, which is time-consuming particularly for the very stable $\alpha\text{-Al}_2\text{O}_3$ modification, being thus circumvented. Fine sample dispersion and efficient stirring ensure a sufficient homogeneity of the suspension. Calibration with a suspension of Al_2O_3 doped with a defined quantity of gallium (embedded in this matrix) is advised, the use of standard aqueous solutions of Ga containing a suspension of Al_2O_3 leading to incorrect results. Minority components in actual samples do not interfere appreciably.

REFERENCES

1. Egorova L. A., Obodynskaya N. V., Sizonenko N. T.: Sb. Nauch. Tr. VNI Monokristallov 11, 106 (1983).
2. Gorlova M. N., Veller N. D.: Zavod. Lab. 48, 31 (1982).
3. Sukhoveeva L. N., Butrimenko G. G., Spivakov B. Ya.: Zh. Anal. Khim. 35, 649 (1980).
4. Anderson J., Van der Walt T. N., Strelow F. W. E.: Geostandards Newslett. 9, 17 (1985).
5. Shan Xiao-quan, Yuan Zhi-neng, Ni Zhe-ming: Anal. Chem. 57, 857 (1985).
6. Slovák Z., Dočekal B.: Anal. Chim. Acta 129, 263 (1981).
7. Samsonov G. V. and coworkers: *Fiziko-khimicheskie svoistva elementov*, p. 214. Naukova dumka, Kiev 1965.

Translated by P. Adámek.