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Determination of macro-constituents in lithium zirconate for tritium-breeding applications

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Abstract

A method was developed for the determination of Li and Zr in lithium metazirconate, a candidate in fusion reactor designs as tritium-breeder material. In order to achieve high-precision results, Li was determined by flame emission spectrometry (FAES) with reduced sensitivity at 610.4nm, whereas Zr was determined by gravimetry and complexometry. The sample was decomposed with NH_4HSO_4. Both elements could be determined to a precision of four significant figures and the Zr results obtained by chemical methods were not significantly different.

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1. Introduction

Lithium-based materials are of fundamental importance for the production of tritium in breeding blankets of fusion reactors. Lithium oxide, sulphate, titanate and zirconate have been considered as ceramic breeder materials [1]. For a number of reasons, such as efficiency in tritium production and subsequent release, lithium metazirconate (Li_2ZrO_3) and also lithium titanate (Li_2TiO_3) are of considerable interest [2,3]. The synthesis of lithium zirconate may be carried out by using different procedures. They include a solid state reaction between lithium peroxide [4] or lithium carbonate [3,5] and zirconium dioxide or a wet reaction between zirconium propylate and lithium acetate [6]. If the physical and mechanical characterisation of Li_2ZrO_3 is important in qualitatively comparing candidate breeder material [3,7], the chemical characterisation of the product is necessary in order to detect an eventual shift from stoichiometry during the process. Being the lithium content of ceramic breeder directly related to the production of tritium, the accurate and precise determination of such constituent has priority. The determination of zirconium is also of interest. Atomic absorption spectrometric techniques are often utilised for lithium determination in different kinds of samples. However, these techniques are rarely so precise as required by the present problem. On the other hand, chemical methods for lithium are often time-consuming, not selective and sometimes inaccurate. A potentiometric method using a fluoride-selective electrode first developed by Baumann [8], then adapted in this Laboratory to the analysis of lithium carbonate [9], cannot tolerate

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zirconium, due to the complexometric reaction with the fluoride. Until now, little attention has been paid to the flame atomic emission spectrometry (FAES) using lines which provide lower sensitivity than the Li 670.8 nm line corresponding to a transition from the first excited state to the ground state. This approach should avoid multiple dilution steps contributing to the uncertainty of the final result. The aim of the present work was to develop a new high-precision method for the determination of lithium and to apply a classical gravimetric procedure using mandelic acid to the determination of zirconium in ceramic breeder. To the best of our knowledge, this reagent, discovered by Kumins [10] and recommended above all other reagents for the determination of zirconium in amounts above 1 mg [11], was not previously applied to the characterisation of lithium zirconate. This one because gravimetric methods, though more accurate and precise than instrumental methods, remain exceptions in laboratory practice for reasons of time and costs. A complexometric procedure using EDTA [12] was also used to control the gravimetric results. This paper will prove that the high-precision determination of macro-constituents in nuclear materials offers new opportunities to the classical methods of analysis.

2. Experimental

2.1. Instrumentation

Flame atomic emission measurements were made with a Perkin-Elmer Mod. 5100 atomic absorption spectrometer with flame emission capability. An acetylene-air flame with a conventional burner head was used. The gas flows were adjusted to obtain maximum signal-to-noise ratio. The instrument was used at 0.4 nm nominal bandpass. The emission intensity was measured at the 610.4 nm lithium atomic emission line. Some preliminary experiments were performed at 323.4 nm. Before processing each series of samples, the gain control was adjusted while aspirating a standard to always provide the same reading.

2.2. Reagents and solutions

All reagents used were of analytical grade (Carlo Erba, Fluka and Merck) and all solutions were prepared with deionized–distilled water. EDTA standard solution was prepared from the Merck concentrate. Working standards of lithium were prepared daily by diluting known aliquots of the Li standard 1000 $\mathrm{mg\,l^{-1}}$ obtained by dissolving Li_2CO_3 with the minimum excess of H_2SO_4 5% v/v (≈25 ml).

2.3. Procedure

2.3.1. Sample preparation

A fusion with ammonium hydrogen sulphate, proposed by Matsumoto et al. [13] to decompose the titanium dioxide and applied by Ashino and Takada [14] to the analysis of lithium niobate, was adequate to attack the zirconate sample. Alternative procedures using $K_2S_2O_7$ or a mixture of sodium carbonate and borax gave less satisfactory results.

Heat the lithium zirconate for 2 h at 800 °C to remove traces of carbon dioxide then cool to the room temperature in a vacuum desiccator. Accurately weigh (±0.02 mg) suitable aliquots of the sample in a Pyrex test tube. For Li determination weigh 30–35 mg, 120–130 mg for Zr by gravimetry, 20–30 mg for Zr by complexometry. Mix the sample with 2 g ammonium hydrogen sulphate (2.5 g for gravimetry). Heat gently to fuse the content then more strongly to fumes of sulphuric acid.

2.3.2. Lithium determination by FAES

Dissolve the cooled melt with 5.0 ml of 1.0 M sulphuric acid by heating at ≈80 °C. Transfer into a 25 ml calibrated flask and adjust the volume with water. Aspirate the solution into the flame and read the emission at 610.4 nm. Determine the lithium concentration by measuring two standards bracketing the unknown.

For standards, fuse 100 mg zirconia with 2.5 g ammonium hydrogen sulphate, dissolve the melt with water and dilute to 50 ml. To 10 ml of the resulting solution add the appropriate amount of lithium sulphate to obtain 110–130 ppm Li after dilution to 25 ml.

2.3.3. Zirconium determination by gravimetry and complexometry

Dissolve the cooled melt with 20 ml of 5% HCl (v/v), then add 50 ml of 16% D,L-mandelic acid (m/v) and dilute to 100 ml with water. Allow the precipitated solution to digest at 85 °C for 25 min and then filter through paper white ribbon. Wash the precipitate repeatedly with hot solution of 5% D,L-mandelic acid (m/v) in 2% HCl (v/v). Transfer the funnel with the filter in an oven, then heat at 110 °C for 1 h. After it is dry, put the filter in a porcelain crucible that has been brought to constant weight and heat on a small Bunsen flame. Char the filter by increasing the flame temperature, then heat the crucible in a muffle at 1050 °C for 2 h. Cool in a vacuum desiccator and weigh to obtain the ZrO_2 by difference. Bring to constant weight.

Dissolve the cooled melt with 50 ml 0.5 M sulphuric acid and add 1.5 g sodium sulphate. Boil the solution for 10 min, dilute with 80 ml water and boil again. Cool to room temperature, then add ≈100 mg of solid xylenol orange. Titrate slowly with 0.01000 M EDTA until the colour changes from red to yellow.

3. Results and discussion

3.1. Effect of different concomitants on the lithium AE signal

It is known that ammonium hydrogen sulphate employed to decompose the lithium zirconate should melt before decomposing to the active sulphuric acid and ammonia at 350–450 °C [13]. However, as the residual unaltered fraction was a potential interferent, the effect of increasing concentrations of ammonium hydrogen sulphate on the Li emission signal at 610.4 nm was investigated. Results reported in Table 1 shown that the signal depression varies between 4% (20 $\mathrm{g\,l^{-1}}$ ammonium hydrogen sulphate) and 12% (120 $\mathrm{g\,l^{-1}}$ ammonium hydrogen sulphate). The precision of repeated ($N = 20$) emission measurements for 100 $\mathrm{mg\,l^{-1}}$ Li in 0.01 M sulphuric acid was 0.2% in terms of RSD whereas in the presence of 100 $\mathrm{g\,l^{-1}}$ ammonium hydrogen sulphate was 0.7%. The effect of zirconium, alone or mixed to other concomitants, was also studied. To quantitatively simulate the lithium zirconate, a calibration curve in the range 0–200 $\mathrm{mg\,l^{-1}}$ Li with a sixfold excess Zr(IV) for each Li standard was constructed. The linear regression parameters for a five-point graph were: $a = (-2.7 \pm 14) \times 10^{-3}$, $b = (2.11 \pm 0.15) \times 10^{-3}$, $r = 0.9997$, 95% confidence. The detection limit ($3s_B$) was 6 $\mathrm{mg\,l^{-1}}$ Li. A statistical comparison with a calibration curve in the absence of zirconium did not reveal any difference in sensitivity ($P = 0.05$) but the precision was poorer.

Table 1
Effect of NH_4HSO_4 on the emission signal of 100 $\mathrm{mg\,l^{-1}}$ lithium

NH_4HSO_4 ($\mathrm{g\,l^{-1}}$)	20	40	60	80	100	120
Rel. emiss. (%)[a]	96	94	92	90	89	88

[a] The relative emission for lithium in the absence of NH_4HSO_4 was normalized to 100%.

Table 2
Effect of various concomitants on the emission signal of 100 $\mathrm{mg\,l^{-1}}$ Li

Concomitant	Concentration ($\mathrm{g\,l^{-1}}$)	Relative emission[a] (%)
H_2SO_4	0.20[b]	98
HNO_3	0.40[b]	100
Zr(IV) + H_2SO_4	0.60 + 0.20[b]	98
Zr(IV) + NH_4HSO_4	0.60 + 80	90
NH_4HSO_4 + HNO_3	100 + 0.40[b]	90
NH_4Cl	46	71
KCl	30	91

[a] The relative emission for lithium in 0.01 $\mathrm{mol\,l^{-1}}$ H_2SO_4 was normalized to 100%.
[b] Concentration in $\mathrm{mol\,l^{-1}}$.

Table 3
FAES determination of lithium added to ZrO_2

ZrO_2 (mg)	Li, added (mg)	Li, found (mg)	Recovery (%)
40.0	23.87 ± 0.02	23.88 ± 0.17[a]	100.0
40.0	23.80 ± 0.02	23.74 ± 0.17	99.7
40.0	23.85 ± 0.02	23.86 ± 0.17	100.0
40.0	23.89 ± 0.02	23.86 ± 0.17	99.9

[a] Uncertainty expressed as standard deviation in reading the Li emission signal ($N = 20$).

Table 4
Comparative determination of zirconium in commercial reagents

Reagent	ZrO_2, expected (% m/m)	ZrO_2, found (% m/m)[a]	
		Gravimetry	Complexometry
$ZrOCl_2 \cdot 8H_2O$ (Fluka)	38.2	38.3 ± 0.3 ($N = 5$)	38.2 ± 0.2 ($N = 3$)
ZrO_2 (RPE-Erba)	$\geqslant$99	99.1 ± 0.3 ($N = 3$)	

[a] 95% Confidence interval.

Table 5
Analysis of lithium zirconate by FAES and chemical methods

Li, found (% m/m)[a]	Zr, found (% m/m)[a]		Li/Zr, found (% mol/mol)[a]	
	Gravimetry	Complexometry	Gravimetry	Complexometry
8.99 ± 0.07 ($N = 5$)	59.04 ± 0.07 ($N = 5$)	59.00 ± 0.10 ($N = 3$)	2.00 ± 0.01	2.00 ± 0.01

[a] 95% Confidence.

Results of further interference studies are reported in Table 2. They show that zirconium in the presence of ammonium hydrogen sulphate significantly depresses the lithium emission (−10%). This may be probably ascribed to the ammonium ion. In fact, a comparison between the effect of ammonium chloride and potassium chloride, with a constant concentration of cation (15.5–15.7 $\mathrm{g\,l^{-1}}$), shows a depressive effect of ammonium chloride around 30%. On the basis of the above experiments, the use of matrix-matched standards is recommended. To strictly reproduce the sample solution, a proper amount of zirconium dioxide was fused with ammonium hydrogen sulphate.

3.2. Accuracy

Since there are no available standard reference materials, recovery tests were performed by adding known amounts of lithium sulphate to the zirconium dioxide before fusion. Results are reported in Table 3. The recovery is between 99.7% and 100.0% for a lithium content simulating that of Li_2ZrO_3. To compare the performance of chemical methods for determining zirconium, two different compounds were repeatedly analysed. Results shown in Table 4 confirm the reliability of the proposed procedure.

3.3. Analysis of real samples

The results of some repeated determinations of lithium and zirconium for a non-sintered Li_2ZrO_3 sample provided by Centro Ceramico (Bologna) are reported in Table 5. Lithium was determined by FAES and zirconium by gravimetry and complexometry. Both elements could be determined to a precision of 0.3–0.7%. Zirconium results obtained by different chemical methods were not significantly different ($P = 0.05$). The atomic ratio (Li/Zr) did not evidence shifting from stoichiometry during the preparation of such tritium breeding compound. The above conclusions show that classical analysis is helpful in the development of new materials and its revival [15] is vital to the interests of industry.

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