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Flow System for Liquid Sample Introduction in Arc/Spark Excitation Sources

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A flow system based on the monosegmented flow analysis (MSFA) approach is described for delivery of liquid samples to arc/spark excitation sources commonly used in spectrographs. A Carl Zeiss PGS-2 spectrograph, previously automated in the laboratory by replacing its photographic plate detection system with a photodiode array, was employed. The sample is introduced *via* an injection port into the path to the excitation source, where the liquid sample plug (typically 50 μl) is passed through a hole drilled in a conventional graphite electrode. The arc/spark is applied to excite the sample for a computer-controlled time interval and the light emitted is integrated. After sample measurement, the electrode is cleaned by applying the arc/spark while the water stream, that follow the sample plug, is being pumped. About 25 samples can be analysed per hour. The flow system was evaluated for determination of aluminium (3–50 mg l^{-1}), lead (5–160 mg l^{-1}) and mixtures of hafnium (60–120 mg l^{-1}) and zirconium (600–1300 mg l^{-1}).

Keywords: *Monosegmented flow system; arc/spark excitation sources; spectrography; aluminium; lead; hafnium; zirconium*

Introduction

Classical emission spectrometry, which employs an arc/spark source for atomization and excitation,[1] can be considered as the predecessor of the modern techniques that use ICP and dc plasmas as excitation sources.[2,3] The detection limits observed for the arc/spark source are worse than those obtained by an ICP or dc plasma-based instrument, mainly owing the poor characteristics of the arc/spark source, such as a lack of reproducibility and stability. However, arc/spark-based spectrometry can still find its place in the analysis of solid samples such as metallic alloys. The operation of an arc/spark instrument is also less expensive and if the lack of sensitivity can be tolerated the technique can prove very useful.

Old spectrographs, constructed to operate with arc/spark sources and to employ a photographic plate as detector, frequently have excellent optics and there have been a number of reports on approaches to update these instruments by using modern detectors, extending their use in routine analysis.[4–6]

Although the use of flow techniques, such as flow injection with ICP and dc plasma instruments has been successfully achieved, owing the characteristics of such sources (developed originally to work with liquid samples aspirated through a nebulizer),[3,7–9] the same is not true for the arc/spark technique. Most procedures reported for the analysis of metallic specimens present in liquid samples by classical spectrography and employing an arc/spark excitation source are based on the use of the rotating disc approach.[10–16] This is, in fact, a batch procedure in which the liquid sample is initially placed in a porcelain cuvette and a film of the liquid sample is then transported to the excitation source. An arc or spark excitation mode can be employed. Another approach employs capillary graphite electrodes to deliver the liquid sample by the vacuum-cup technique. These techniques should be also classified as batch procedures.[17,18]

So far, no flow system seems to have been developed with the intention of delivering liquid samples to spectrographs that employ arc/spark excitation sources. Such a system could improve the sample throughput of automated spectrographs that employ arrays of solid-state sensors such as multichannel detectors and allow one to work with small volumes of sample.

This paper describes a flow system developed to automate the delivery of liquid samples to arc/spark excitation sources commonly used with plane grating spectrographs. The performance of the system and the important flow and instrumental variables were investigated with the aim of determining aluminium, lead and mixtures of hafnium and zirconium in aqueous solution.

Experimental

Instrument

A Carl Zeiss Model PGS-2 spectrograph whose automation has recently been described was employed.[4] The instrument has a 1024-element diode-array sensor and is fully automated. Data acquisition and control of the excitation source are made under microcomputer control through a laboratory-made computer interface.[4] The diode-array sensor can observe a spectral output window of about 18.7 nm in the first order of the diffraction grating (7 × 6 cm, 651 grooves mm^{-1}, blazed at 550 nm) usually employed in the spectrograph. Light emitted by the source can be integrated for 1–40 s using the Peltier-cooled sensor array.[4]

Flow System

Fig. 1 shows the flow system proposed for liquid sample delivery to the excitation source of the spectrograph. PTFE tubing of 0.8 mm id is used throughout. The injection valve is shown in the sampling position. While in this position air is being pumped through the tubing connecting the valve to the graphite electrode. When moved forward, to the injection position, 50 μl of the sample are introduced into the air stream followed by an air segment of 450 μl and then by a de-ionized water stream that flows while the valve remains in the injection position. The flow pattern acquires the characteristics of a monosegmented flow analysis (MSFA) system in which the sample is carried to the detector between two air bubbles.[19] When the valve is returned to collect another sample, the water present in the path to the electrode is removed by the air stream.

In a graphite electrode, 5 cm × 0.7 cm diameter, an axial hole (0.6 mm diameter) is drilled and through this hole a quartz tube (0.4 mm id, 0.5 mm od) is fixed using epoxy cement. The PTFE

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tube that connects the electrode to the injection valve is fitted directly to the end of the quartz tube, at the bottom of the electrode. The other end of the electrode is polished to obtain a flat surface. The excitation system also employs a conventional graphite counter electrode. The injection system has an optical switch that indicates to the computer when the valve is moved to the sample introduction position, allowing the software to process the necessary operations for data acquisition and instrument control.

Instrument Control and Data Acquisition Procedure

The grating of the instrument is initially positioned so that the wavelength window of interest, for a given analyte, is able to be monitored by the diode-array detector. The operations that follow the sample introduction are shown in the flow diagram in Fig. 2. At the end of the cycle the electrode is cleaned and dried, ready to process another sample. The most important variables to be optimized in the system are the time intervals: t_w = waiting time, t_h = pre-heating time, t_i = signal integration time, t_f = water flush time interval and t_c = cleaning time interval.

Data Evaluation for Quantitative Determination

The determination of the analyte present in the aqueous solution introduced into the system was performed by using Fe or K as internal standard. The analytical parameter was always the ratio of the integrated intensities taken between a characteristic and intense emission line of the analyte and a line of the internal standard found in the same spectral window accessed by the array of sensors.

The integrated intensity was obtained by summing the intensities of the diodes embodied by the emission lines of interest. The developed software allows for the selection of the line of interest for the analyte and that for the internal reference and obtains the integrated intensity and the ratio for construction of the calibration curve and/or determination of the analyte.

For the determination of mixtures of hafnium and zirconium the data processing takes into account the interference of zirconium emission (339.94 nm) in the hafnium spectral line (339.98 nm). The contribution of the presence of zirconium in the hafnium spectral line is first established by using standard solutions that contain only zirconium and looking for the signal in the hafnium emission line. The determination procedure finds the zirconium content of the sample and removes its contribution (interference) from the hafnium signal.

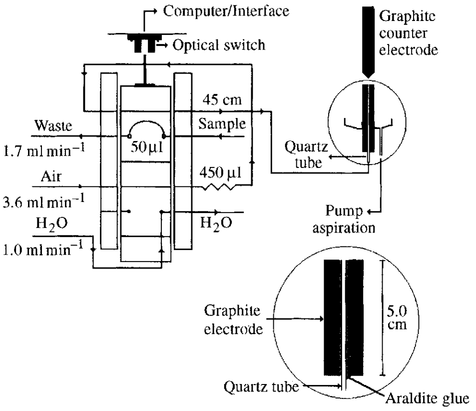

Fig. 1 Flow system proposed for liquid sample presentation to arc/spark excitation source. Values of the flow parameters are typical for the determinations carried out in this work.

Reagents and Solutions

Stock standard solutions containing 1000 mg l^{-1} of Pb^{II} and Al^{III} and 5000 mg l^{-1} of Fe were prepared from the metals following standard procedures.[20] The solutions of the Al^{III} and Pb^{II} were prepared in 0.1 mol l^{-1} hydrochloric acid and nitric acid, respectively. A 2500 mg l^{-1} potassium stock standard solution was prepared from dried potassium nitrate.

Stock standard solutions of Zr and Hf were prepared from $ZrCl_2 \cdot H_2O$ and metallic hafnium, respectively. Both solutions were standardized by employing a recommended gravimetric method where hafnium and zirconium were precipitated as their tetramandelates.[21,22]

Results and Discussion

Optimization of the Flow System

Initially the optimum conditions for the continuous current spark excitation source were found to be 500 µH, 25 µF and 6 Ω, and were about the same for all specimens studied. A slit aperture of 100 µm was employed and the other parameters were optimized.

Fig. 3 shows the effect the water carrier flow rate on the intensity of the aluminium signal at 396.15 nm. Flow rates

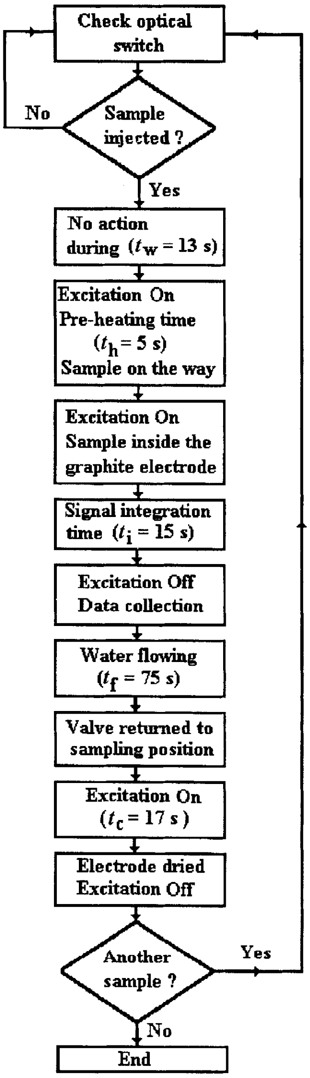

Fig. 2 Flow chart showing the sequence of operations necessary to perform a determination by using the proposed flow system. Time intervals shown are typical for the determinations performed in this work.

above 1.0 ml min^{-1} decrease the signal of aluminium, probably because the sample plug is delivered to the excitation region at a rate that causes a loss of energy of the source due the high intake of aqueous solution. The flow rate selected for subsequent experiments was 1.0 ml min^{-1}.

Fig. 4 shows the effect of the sample volume on the intensity of the aluminium signal. An integration time of 15 s is sufficient to maintain the excitation source switched on during the passage of a sample plug of up to 250 µl at a water carrier flow rate of 1.0 ml min^{-1}. However, the signal decreases when the sample volume is increased above 50 µl. Again, the loss of energy of the source, caused by an excess of aqueous solution, can explain the observed behaviour of the signal.

The effect of the integration time on the ratio of the integrated signals of Al and Fe for a 50 µl sample volume reaches a steady value at integration time intervals above 7 s, as shown in Fig. 5. A value of 15 s was chosen because it is more effective in removing the metal from the electrode surface avoiding memory effects. Higher integration time intervals should be avoided in view of the increase in the dark current of the diode array that limits the dynamic range of the detection system.[4]

The pre-heating time interval during which the excitation source is on, while the sample is still on the way to the electrode, also has some effect on the analytical signal, as shown in Fig. 6. A minimum of 5 s should be established for the pre-heating time in order to obtain the maximum signal.

Although optimized for aluminium determination, using Fe as internal standard, the timing parameters were found to be the same for Pb, Hf and Zr. The effect of matrix modifiers has not been evaluated and, perhaps, the use of such substances could affect the time-related parameters of the flow spark/system.

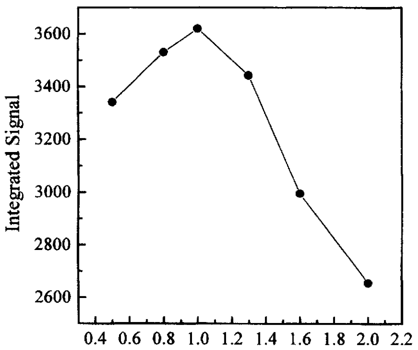

Fig. 3 Effect of the water carrier flow rate on the integrated intensity of the aluminium signal at 396.15 nm. Sample volume, 50 µl; pre-heating time, 5 s; integration time, 15 s; Al^{III} concentration, 50 mg l^{-1}.

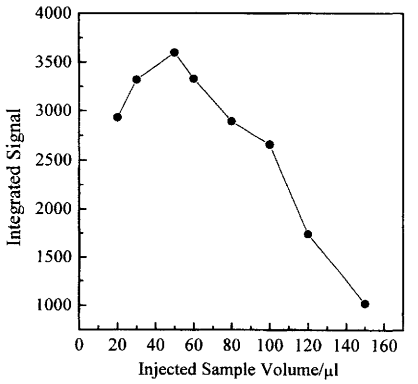

Fig. 4 Effect of the sample volume injected on the integrated signal for aluminium. Pre-heating time, 5 s; integration time, 15 s; carrier flow rate, 1.0 ml min^{-1}; Al^{III} concentration, 50 mg l^{-1}.

Memory Effects

Memory effects were observed when very concentrated solutions were processed by the flow system. This effect was observed when a 50 mg l^{-1} Al^{III} solution was introduced followed by a low-concentration solution (3 mg l^{-1}) and when solutions containing high concentrations of Zr (> 1000 mg l^{-1}) were introduced in order to determine a low content of Hf. To avoid this problem, an aqueous solution is introduced in place of the sample before a lower concentration sample is analysed.

Calibration Curves for Al^{III} and Pb^{II}

The calibration curves for Al^{III} and Pb^{II} were obtained by introducing 50 µl of standard solutions of the metals containing 1000 mg l^{-1} of Fe and K, respectively, as internal standard. A linear relationship between the ratio of the integrated signals (analyte/internal standard) and analyte concentration was observed and relevant statistical parameters are given in Table 1 for calibration curves obtained by using six standard solutions.

Determination of Mixtures of Hafnium and Zirconium

The determination of Hf and Zr in mixtures is important, for example, in order to follow the efficiency of separation methods developed to obtain one of the metals in the absence of the other. Although the chemical properties of these elements are very similar, the physical properties such as neutron absorption are completely different. For example, zirconium used in nuclear applications must contain hafnium at a level below 0.1%.[23,24]

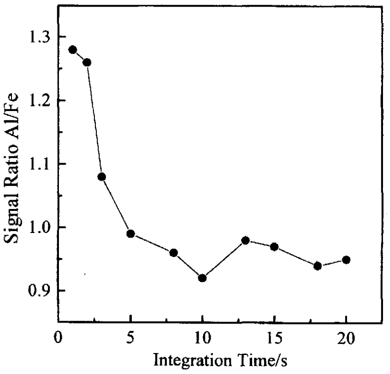

Fig. 5 Change in the analyte internal standard signal ratio (Al/Fe) caused by increasing the integration time. A minimum of 7 s is necessary to achieve good stability. Pre-heating time, 5 s; carrier flow rate, 1.0 ml min^{-1}; sample volume, 50 µl; Al^{III} concentration, 50 mg l^{-1}.

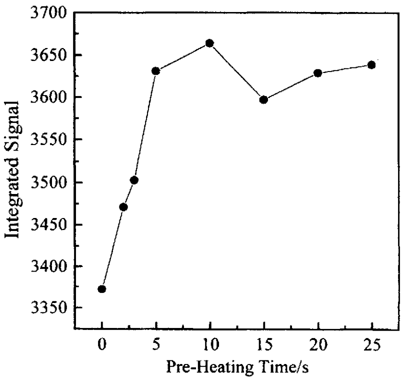

Fig. 6 Behaviour of the integrated signal for aluminium in the determination of the pre-heating time interval. Carrier flow rate, 1.0 ml min^{-1}; integration time, 15 s; sample volume, 50 µl; Al^{III} concentration, 50 mg l^{-1}.

Initially the spectral region possible to be monitored by the automated spectrograph[4] was scanned, looking for intense emission lines of Hf and Zr. The lines at 339.20 nm for Zr and 339.98 nm for Hf revealed some good characteristics. The Fe emission line at 344.06 nm was also found suitable as an internal reference. Further, it was observed that these lines show greater intensity when measured in the second order of the plane grating employed by the instrument. Fig. 7 shows the relevant emission lines obtained for both metals, observed in the second order of the grating. It is possible to observe that even with the greater resolution obtained, by looking at the second-order region the emission line at 339.98 nm due Hf is overlapped by the low-intensity emission line of Zr at 339.94 nm. Therefore, the direct determination of low contents of Hf in the presence of large excess of Zr is subject to reasonable spectral interference.

The proposed method for determining Zr and Hf mixtures where the first metal is present in large excess in relation to the second has three stages: (i) Hf is determined using the integrated intensity of its line at 339.98 nm; (ii) the interference caused by the Zr in the Hf emission line is determined; and (iii) the sample is diluted 30-fold and Zr is determined by using the integrated intensity of its emission line at 339.20 nm. In all determinations the ratio between the integrated signal produced by the metal and that produced by a 1500 mg l^{-1} solution of Fe (at 344.06 nm) is employed.

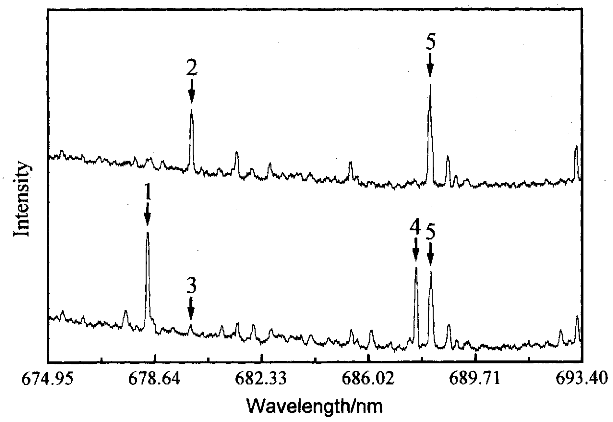

Fig. 7 Two emission spectra obtained for solutions of hafnium and zirconium, containing iron as internal standard, showing some characteristic emission lines. 1, Zr line at 339.20 nm; 2, Hf line at 339.98 nm; 3, low-intensity Zr line at 339.94 nm; 4, Zr line at 343.82 nm; and 5, Fe line at 344.06 nm used as reference. The wavelength scale is shown as it should be if the first order spectrum is being recorded. Zr and Hf concentrations, 70 and 85 mg l^{-1}, respectively.

Table 2 shows that the ratio of the integrated signals, necessary to perform the three-stage determination of Hf and Zr mixtures, is linearly related to the concentration of Hf in Zr.

Table 3 shows the results, taken before and after correction, obtained for the determination of Zr and Hf in mixtures. All results are presented with their relative standard deviations, derived from the average of four measurements. Errors as great as 143% can be reduced to 8.6% after correction due the spectral interference of Zr in Hf determination.

Conclusion

The use of modern multichannel detectors with computer-assisted spectrographs allow more reproducible and faster flow systems to be employed to deliver liquid samples to arc/spark excitation sources. The approach described here employs sample volumes as low as 50 µl while being capable of achieving the same sensitivity as reported for other batch sampling procedures previously applied along with ark/spark excitation sources. The adaptation necessary to conventional excitation equipment in order to work with the proposed flow system is very simple and inexpensive. The system proposed has demonstrated good performance when applied to the determination of Al, Pb, Hf and Zr present in aqueous solutions. The sample processing capability of the system (25 h^{-1}) and the use of the same modified graphite electrode to perform up to 80

Table 3 Results obtained before and after correction (n = 4) for the determination of Zr and Hf in mixtures

Concentration taken/mg l^{-1}		Concentration found/mg l^{-1} [± RSD/relative difference (%)] without correction		Concentration of Hf found/mg l^{-1} [± RSD/relative difference (%)] after correction
Zf	Hf	Zr	Hf	
611	67	619 (±2.8/+1.3)	149 (±1.9/+122)	60 (±3.2/−10)
785	70	781 (±1.7/−0.5)	170 (±2.9/+143)	64 (±4.3/−8.6)
873	126	879 (±2.3/+0.7)	235 (±1.8/+87)	120 (±2.6/−4.8)
1309	126	1332 (±2.7/+1.8)	281 (±2.4/+123)	119 (±2.1/−5.5)

Table 1 Statistical parameters for the calibration curves obtained for Al and Pb. Sample volume, 50 µl; other parameters as in Fig. 1

Metal	Concentration range/mg l^{-1}	Slope ± s	Linear coefficient ± s	Correlation coefficient	Standard deviation of the fit
Al	3–50	0.0189 ± 0.0003	0.040 ± 0.008	0.9994	0.019
Pb	5–160	0.0086 ± 0.0001	0.035 ± 0.009	0.9995	0.017

Table 2 Statistical parameters for the calibration curves obtained for Zr and Hf in mixtures. Sample volume, 50 µl; other parameters as in Fig. 1

Metal	Emission line/nm (line of metal)	Concentration range/ mg l^{-1}	Slope ± s	Linear coefficient ± s	Correlation coefficient	Standard deviation the fit
Zr	339.20 (Zr)	10–70	0.0135 ± 0.0002	0.055 ± 0.008	0.9996	0.010
Hf	339.98 (Hf)	42–125	0.00415 ± 0.00004	−0.076 ± 0.029	0.9998	0.002
Zr	339.98 (Hf)	262–1500	0.00044 ± 0.00005	0.096 ± 0.004	0.9997	0.003

determinations are also positive aspects of the proposed method. So far the adjustment of the electrode position in the excitation source, made after each ten determinations, has been made manually. However, in the future a simple stepper motor could be used to replace the original position of the electrode after a certain number of determinations.

The main achievement of the proposed flow system is in the inexpensive automation of spectrographs to allow liquid sample delivery to the arc/spark source. The limitations of such an excitation source, as the lack of reproducibility, are well known. Therefore, although the proposed flow system can improve some of the characteristics of the arc/spark system and make it more versatile, the sensitivity achieved is lower than that obtained with modern excitation sources as ICP and dc plasmas. On the other hand, the fact that the proposed system requires a very small volume of sample (50 μl) suggests its use after preconcentration procedures that could be used to improve the detection limits of the arc/spark liquid sample delivery system.

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References

1 Török, T., Mika, J., and Gegus, E., *Emission Spectroscopic Analysis*, Adam Hilger, Bristol, 1978.

2 Moore, G. L., *Introduction to Inductively Coupled Plasma Atomic Emission Spectrometry*, Elsevier, New York, 1989, vol. 3.

3 Boumans, P. W. J. M., *Inductively Coupled Plasma Emission Spectroscopy, Part I*, Wiley-Interscience, New York, 1987.

4 Bellato, C. R., Rohwedder, J. J. R., Raimundo, I. M., Jr., and Pasquini, C., *J. Autom. Chem.*, 1996, **18**, 7.

5 Brett, L., Kalsi, A., Cummins, S., and Thombs, D., *Anal. Proc.*, 1991, **28**, 224.

6 Brett, L., Stahl, R. G., and Timmins, K. J., *J. Anal. At. Spectrom.*, 1989, **4**, 333.

7 Hinds, M. W., and Valente, F., *Can. J. Appl. Spectrosc.*, 1995, **40**, 89.

8 Fairman, B., Sanz-Medel, A., and Jones, P., *J. Anal. At. Spectrom.*, 1995, **10**, 281.

9 de Andrade, J. C., and Bueno, M. I. M. S., *Spectrochim. Acta, Part B*, 1994, **49**, 787.

10 Kántor, T., Erdey, L., and Szabó-Ákos, Zs., *Talanta*, 1970, **17**, 1199.

11 Ondrick, C. W., Suhr, N. H., and Medlin, J. H., *Appl. Spectrosc.*, 1969, **23**, 111.

12 Suhr, N. H., and Ingamells, C. O., *Anal. Chem.*, 1966, **38**, 730.

13 Kopp, J. F., and Kroner, R. C., *Appl. Spectrosc.*, 1965, **19**, 155.

14 Eardley, R. P., and Clarke, H. S., *Appl. Spectrosc.*, 1965, **19**, 69.

15 Paolini, A., Jr., and Kennedy, R. M., *Appl. Spectrosc.*, 1962, **16**, 15.

16 Heller, H. A., and Lewis, R. W., *Anal. Chem.*, 1953, **25**, 1038.

17 Delijska, A., *Fresenius' Z. Anal. Chem.*, 1982, **312**, 523.

18 Bevege, E. E., and Gallion, R. E., *Appl. Spectrosc.*, 1967, **21**, 20.

19 Pasquini, C., and Oliveira, W. A., *Anal. Chem.*, 1985, **57**, 2575.

20 Vogel, A. I., *A. Textbook of Quantitative Inorganic Analysis Including Elementary Instrumental Analysis*, Longman, London, 1978.

21 László, E., *Gravimetric Analysis Part II*, Pergamon Press, Oxford, 1965, pp. 474–486.

22 Barbiéri, R. S., Rocha, J. C., Terra, V. R., and Marques, A., *Eclética Quím.*, 1989, **14**, 101.

23 Mukherji, A. K., *Analytical Chemistry of Zirconium and Hafnium*, Pergamon Press, Oxford, 1970.

24 Clark, R. H., Bradley, D. C., and Thornton, P., *The Chemistry of Titanium, Zirconium and Hafnium*, Pergamon Press, Oxford, 1975, pp. 419–486.

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