Selectivity enhancement in spectrophotometry: on-line interference suppression using polyurethane foam minicolumn for aluminum determination with Methyl Thymol Blue

The Analyst

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A method is proposed for the determination of aluminum by flow injection spectrophotometry with Methyl Thymol Blue after separation of the interferent ions employing a polyurethane foam (PUF) minicolumn. The separation process is based on the retention of the interferents on the PUF minicolumn as thiocyanate complexes. In order to improve the performance of the system the effect of some chemical and flow variables were evaluated and under optimized conditions the system was able to determine aluminum at a concentration of 1.0 µg mL^{-1} in the presence of Fe(III) at 170 µg mL^{-1}, Zn(II) at 100 µg mL^{-1} and Cu(II) and Co(II) at 50 µg mL^{-1}, using a PUF minicolumn containing 200 mg of sorbent. The analytical procedure developed was successfully applied to several certified materials, including silicate materials and ores. Very good accuracy and precision was obtained. A limit of detection of 30 ng mL^{-1} was achieved with RSD of 4.5% at 0.25 µg mL^{-1}. A linear dynamic range from 0.25–2.0 µg mL^{-1} was observed and a sample frequency of 17 samples per hour was calculated.

1 Introduction

Automation in analytical chemistry has assumed importance in the last few years due to the development of continuous separation techniques. Separation techniques carried out in a continuous way are based on mass transfer processes between solid–liquid, solid–gas, liquid–liquid or liquid–gas interfaces.[1] Solid–liquid systems have been commonly used as solid phase extraction (SPE) for separation or analyte preconcentration. Several sorbents have been employed such as C-18, C-8, C-2 bonded silicas, styrene–divinylbenzene copolymers (XAD-2), activated alumina and activated carbon[1] and polyurethane foams (PUF).[2] Polyurethane foams have been employed for sorption and separation of inorganic and organic species from different media.[2] Some reviews about the use of PUF in batch separation and preconcentration procedures have been published which report its applications in the unloaded form[3–5] and as support for reagent immobilization and liquid ion exchangers.[6–9]

On the other hand, due to its own features, flow-injection analysis (FIA) has been used to automate separation and preconcentration procedures with advantages such as: high analytical throughput, good precision and accuracy, low reagent and sample consumption.[10–12] However, as in spectrophotometric determinations, the available reagent often lacks selectivity, and therefore requires a previous separation process.

Recently, SPE using PUF has been adapted for continuous operation and coupled to FIA. A simple and accurate procedure was developed to preconcentrate and determine zinc in biological matrices, using a polyether type PUF. In this system zinc was collected from aqueous media as zinc–thiocyanate complex. Spectrophotometry with 4-(2-pyridylazo)-resorcinol (PAR) was used for the measurement within a dynamic range from 20 to 100 ng mL^{-1} and a detection limit of 0.9 ng mL^{-1} was achieved for 1 min of preconcentration time.[13] In another flow system, nickel was quantitatively separated from iron, copper, zinc and cobalt using a PUF minicolumn, and determined in brass, bronze and silicate materials. A sample throughput of 24 samples per hour was achieved. The separation was based on the retention of interferent ions on the PUF minicolumn as their thiocyanate complexes. The detection limit was found to be 77 ng mL^{-1}. It was possible to sorb 160 µg of Fe and Cu and 80 µg of Zn and Co in 125 mg of unloaded PUF.[14]

Bai and Lu[15] reported an on-line spectrophotometric analytical procedure for Au determination in ores, after its collection on PUF columns. The calibration graph was linear between 0.5 and 6 µg of Au and the detection limit was 0.3 µg.

This present paper reports the use of unloaded polyurethane foam as solid sorbent for spectrophotometry selectivity enhancement. An interference suppression procedure in a continuous flow mode was developed and applied to aluminum determination in silicate and iron ore materials. Methyl Thymol Blue (MTB) was used as colorimetric reagent according to a previous study reported by Ferreira *et al.*[16]

2 Experimental

2.1 Apparatus

A Micronal B-342 II (São Paulo, Brazil) spectrophotometer equipped with a Hellma (Jamaica, NY, USA) flow cell (178-010-OS, inner volume of 80 µL) set at 528 nm was used, coupled to a Chessell (Worthing, Sussex, UK) *x-y* recorder. An Ismatec (MP-13R, Zürich, Switzerland) and Milan (Curitiba, Brazil) peristaltic pumps, supplied with standard PVC tubes, were used to propel all solutions. Rheodyne (Cotati, CA, USA) four way valves were used to switch the separation/loading and

measurement/cleaning steps. All connections were made using PEEK and plastic materials. The manifold was built up with PTFE tubes of 0.5 mm bore.

2.2 Reagents and solutions

Milli-Q Water System (Millipore, Milford, MA, USA) water was used to prepare all solutions. All reagents were analytical grade and were used as received.

Aluminum(III) solutions were prepared by adequate diluting of 1000 µg mL^{-1} aluminum solution (atomic absorption; Aldrich, Milwaukee, WI, USA), using a 5% hydrochloric acid solution.

A 0.2% MTB (Vetec, Rio de Janeiro, Brazil) solution was prepared by dissolving 0.2 g of the reagent in 100 mL of 2.0 mol L^{-1} acetate buffer solution of pH 4.25.

A 1.0 mol L^{-1} thiocyanate solution was prepared by dissolving 24.30 g of KSCN (Vetec) in water, the pH was adjusted to 1.3 with diluted HNO$_3$ and after this the volume was made up to 250 mL.

Polyurethane foam (PUF) open cell, polyether type, was made from the commercial product (made by Atol, Salvador, Brazil). In order to prepare PUF for use as a sorbent, the foam was ground in a blender with demineralized water and washed with 6 mol L^{-1} HCl.[16] A minicolumn was packed with 200 mg of PUF in a small plastic tube of 7.0 cm length × 3 mm id.

2.3 Sample preparation

Dissolution of the samples was achieved by lithium metaborate fusion, using an equimolar mixture of lithium carbonate and boric acid (Merck, Rio de Janeiro, Brazil). A portion of 100 mg of sample was weighed and mixed with 700 mg of such flux. After mixing using a vibrator mill, it was transferred to a platinum crucible and placed in a preheated electric furnace at 950 °C for 15 min. Then the mixture was homogenized and placed again into the furnace kept at the same temperature for a further 15 min. After cooling, the residue was dissolved in 4 mL of concentrated HNO$_3$ (Merck) and 70 mL of water, and further diluted to 100 mL with water. The solution samples were stored in polypropylene flasks and analyzed according to the developed procedure. At least one blank solution was analyzed with the samples to minimize reagent contamination.

Sample decomposition employing acid treatment (HF + HClO$_4$) was not possible due to the presence of fluoride in the remaining solution. A strong interference occurred caused by the formation of aluminum–fluoride complexes, which could not be suppressed. Thus, samples containing appreciable amounts of fluoride cannot be analyzed by this methodology.

2.4 Flow injection system

A schematic diagram of the flow system is depicted in Fig. 1. In this system, a sample solution pumped at 6.7 mL min^{-1} merged with 1.0 mol L^{-1} thiocyanate solution stream at a flow rate of 0.43 mL min^{-1} and percolated through the minicolumn. Interferent ions were sorbed on the PUF minicolumn as thiocyanate complexes and the remaining solution that contained Al(III) (not sorbed in the PUF minicolumn because Al(III)–thiocyanate complex was not formed) filled the sample loop. This step (separation and loading) was carried out in 90 s. Afterwards valves were switched and the measurement and cleaning step started. Sample was displaced from the loop by a water carrier stream pumped at 1.2 mL min^{-1}, merged with reagent at a flow rate of 0.1 mL min^{-1} and mixed with a 200 µL (100 cm) reactor coil placed into a thermostatic bath set at 60 °C. Afterwards the absorbance signals (peak height) were

measured at 528 nm. Simultaneously, a cleaning solution (EtOH–H$_2$O, 1 + 1 in 1% HCL) stream was pumped in the minicolumn at 3.5 mL min^{-1} flow rate, preparing it for a new separation cycle. The time required for an efficient cleaning was 2 min. The sample solutions and the analytical standard solutions were injected into the flow system in the same way.

3 Results and discussion

3.1 Flow system optimization

The main purpose of the developed FIA system was to separate several interferent species for selectivity enhancement and determine aluminum(III) with MTB in many kinds of samples. A PUF minicolumn coupled to a FIA system was thus used to overcome the poor reagent selectivity. In order to improve the separation and measurement performances of the proposed system, both chemical and flow conditions were optimized.

The influence of the pH on the absorbance signals produced by the analyte was studied ranging from 0.1 to 3.1, and this variable did not influence the signals. pH values over 3.1 were not tested since hydroxides (particularly iron) commonly present in the samples could be precipitated in sample solutions.

MTB concentration was studied in a range from 0.025 to 0.4%. Best results were found for MTB concentrations higher than 0.2%. However, in concentrations higher than 0.3% MTB gave rise to baseline noise. For further experiments, a concentration of 0.2% was chosen. The effect of the reagent pH was also studied. Results showed that the absorbance signal is at a maximum at pH 4.25 and for this reason an acetate buffer solution was chosen.

The composition of the cleaning solution for the minicolumn regeneration was also studied. Several solutions containing different concentrations of HNO$_3$, HCl and ethanol were tested and best results were found by using 50% ethanol in 1% HCl solution. Two minutes were enough to clean the minicolumn at a flow rate of 3.5 mL min^{-1}. Flow rates higher than the chosen one did not increase the cleaning and caused a small overpressure inside the minicolumn. Also, in solutions containing more than 50% ethanol the lifetime of the PVC pumping tubes decreased too much.

The effect of the reagent flow rate was studied in the range from 0.03 to 0.32 mL min^{-1}. Best results were verified at 0.1 mL min^{-1}.

The carrier flow rate was tested between 0.8 and 2.0 mL min^{-1}. When the flow rates increased, the signals decreased slightly, maybe due to the slow reaction kinetics. Therefore, a
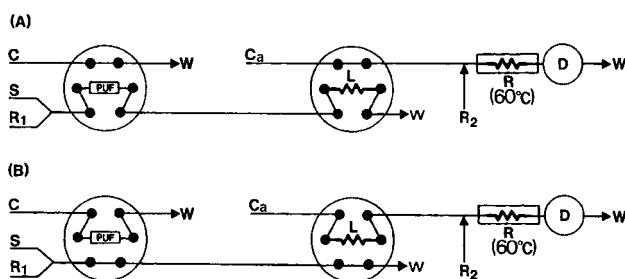

Fig. 1 Flow system manifold for aluminum(III) spectrophotometric determination after separation of interferent cations by solid phase extraction with unloaded polyurethane foam minicolumns. (A) Loading step and (B) measurement step. Ca = carrier, water (1.2 mL min^{-1}); C = cleaning solution, EtOH–H$_2$O 1 + 1 in 1% (v/v) HCl (3.5 mL min^{-1}); S = sample (6.7 mL min^{-1}, pH = 1.3); R$_1$ = 1 mol L^{-1} KSCN (0.43 mL min^{-1}, pH = 3.0); R$_2$ = 0.20% MTB in acetate buffer (0.10 mL min^{-1}, pH = 4.25); L = sample loop (200 µL); R = reactor coil (200 µL) immersed in a thermostatic bath at 60 °C; PUF = polyurethane foam minicolumn (200 mg); D = spectrophotometric detector (528 nm); W = waste.

flow rate of 1.2 mL min^{-1} was chosen to optimize both analytical throughput and sensitivity.

Influence of the reactor coil temperature was investigated (in the presence and in the absence of SCN$^-$) because the rate of the spectrophotometric reaction is slow. In this study, the reactor was immersed in a thermostatic bath kept at temperatures ranging from 25 to 70 °C. It was observed that the increase of temperature made the analytical signals higher. For temperatures over 70 °C bubbles were formed that increased the baseline noise. Since there was only a small difference between the signals achieved at 70 °C and 60 °C, a temperature of 60 °C was chosen.

Sample loops between 50 and 400 μL were studied for the chromogenic reaction. For the best signal, a sample loop of 200 μL was used for further experiments. Influence of the reactor volume on the performance of the system was also tested using coiled reactors with volumes between 100 and 400 μL inside and outside of the thermostatic bath. At room temperature the best absorbance signals were verified with a reactor of 300 μL, while at 60 °C the absorbance was maximized in a reactor volume ranging from 100 to 200 μL. For further experiments, a reactor with a volume of 200 μL was employed.

3.2 Interference and selectivity studies

Retention of interferents on the PUF minicolumn is dependent on the pH, since thiocyanate complex formation is influenced by this parameter. Therefore, the best pH condition was studied for each cation regarded as a potential interferent. According to a previous study,[13] the best retention conditions for some cations were set at 1.0 mol L^{-1} thiocyanate solution concentration and pH 3.0. However, the influence of the sample pH in the retention of each interferent cation was studied using a minicolumn containing 200 mg of PUF. In more acidic conditions (pH 0.1–0.5) some interferences were observed when iron(III) and zinc(II) were present, maybe due to low availability of thiocyanate anion in solution, which brought about a low rate for complex formation. This effect was not observed for cobalt(II) and copper(II). For copper(II) a small increase of the analytical signal was observed when the pH was higher than 1.5. The best pH range to improve selectivity was from 0.5 to 1.5. This way a sample pH of 1.3 ± 0.2 was chosen for the analytical procedure.

In the interference study, one of the most important parameters was the time needed to fill the sample loop. It was tested between 30 and 120 s (6.7 mL min^{-1} sample flow rate) for several concentrations of Fe(III) as interferent cation, since this element is usually found in environmental matrices, particularly in the certified samples that were tested. As can be seen in Fig. 2A, times up to 50 s were not enough to fill up the sample loop, generating aluminum absorbance signals lower than those possible. These signals achieved their maximum values between 60 and 90 s and then kept constant values for solutions containing Fe(III) concentrations up to 100 μg mL^{-1} (Fig. 2B).

Interferences were observed in two distinct situations: when the concentration of Fe(III) was increased up to 200 μg mL^{-1} and when the time of the loading step was higher than 90 s, for concentrations of Fe(III) of 100 μg mL^{-1}. In both cases the minicolumn capacity was extrapolated, bringing about a serious increase in the absorbance signal due to the presence of the Fe(III) inside the sample loop. This way, in order to keep the flow system with a good selectivity without loss of analytical throughput, a filling loop time of 60 s was used for samples containing at least 100 μg mL^{-1} Fe(III). In samples containing 200 μg mL^{-1} of Fe(III), serious interferences can appear in the aluminum signal because the retention capacity of the minicolumn is overcome before filling the sample loop. In this specific situation, the selectivity of the methodology can be

improved by using a time of 30 or 40 s to fill the sample loop which, in its turn, decreases the sensitivity.

Experiments carried out with the flow system operating without the PUF minicolumn (by injection of solutions containing each one of the interferent species) showed that iron(III), copper(II), zinc(II) and cobalt(II) are potential interferent cations because they react with MTB to form complexes that absorb light in the set wavelength. From this point of view, manganese(II) and cadmium(II) cannot be regarded as interferent species. Table 1 shows the cation concentrations that actually interfere in the 1 μg mL^{-1} aluminum signal using a flow system with and without the PUF minicolumn. Interference was considered when a signal difference greater than 10% was observed. From the data in Table 1 it is possible to see that the selectivity enhancement factor (ratio between maximum concentrations that can be tolerated in the flow systems with and without the PUF minicolumn) for iron(III) is very high, which provides a procedure good enough for aluminum spectrophotometric determination in iron matrices. Results obtained for several interferent/analyte ratios are summarized in Table 2.

This system can be applied for the suppression of any interferent metal ion which forms thiocyanate complexes since these complexes are extracted by the foam in the optimized conditions [Fe(III), Zn(II), Mn(II), Cd(II), Co(II) and Cu(II)]. Possible interferents might be listed as metals which do not form thiocyanate complexes and react with MTB, forming
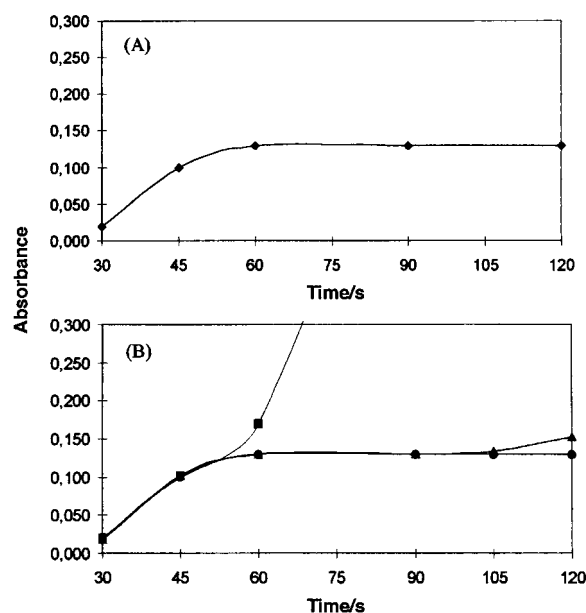

Fig. 2 Effect of time to fill the sample loop with: (A) 1 μg mL^{-1} Al(III) solution (◆) and (B) 1 μg mL^{-1} Al(III) solution in the presence of 50 μg mL^{-1} of Fe(III) (●), 100 μg mL^{-1} of Fe(III) (▲) and 200 μg mL^{-1} of Fe(III) (■).

Table 1 Maximum tolerable concentrations of interferent cations and calculated selectivity enhancement factors considering signal variations of Al(III) solutions of 1 μg mL^{-1}

Interferent	Without PUF minicolumn/ μg mL^{-1}	With PUF minicolumn/ μg mL^{-1}	Selectivity enhancement factor
Fe(III)	0.14	170	1215
Zn(II)	2	100	50
Co(II)	0.6	50	83
Cu(II)	0.75	50	67
Cd(II)	50	—[a]	—
Mn(II)	150	—[a]	—

[a] It was not tested because the reaction between Mn(II) and Cd(II) with MTB is not appreciable.

species that absorb at the set wavelength, such as V(v) and Ti(IV). However, their presence in the samples is negligible compared to the amount of aluminum.

3.3 Analytical features

The flow system developed was able to produce analytical curves with good linearity in the range of 0.25–2.0 mg L^{-1}, with typical equation such as $A = 0.135$ [Al (µg mL^{-1})] -0.002, $r = 0.999$. The detection limit evaluated as three times the standard deviation was found to be 30 ng mL^{-1} and the RSD was 4.5%, assessed by twelve measurements of the standard solution with a concentration of 0.25 µg mL^{-1}. Under optimized conditions, the FIA system was able to process 17 samples per hour.

4 Applications; reference material analysis

In order to study the applicability of the proposed methodology, the content of aluminum was determined in several certified material of rocks (JR-1, GSJ; BIR-1, USGS; AGV-1, USGS; RGM-1, USGS; STM-1, USGS) from Geological Survey of Japan (GSJ, Ibaraki, Japan) and United States Geological Survey (USGS, Reston, VA, USA) and iron ores (IPT-21A, IPT-23A and IPT-27) supplied by Instituto de Pesquisas Tecnológicas (IPT, São Paulo, Brazil), containing different amounts of interfering elements. Achieved results found by the use of the developed procedure for aluminum determination are shown in Table 3. Statistically, all certified values are within the calculated confidence limits (applying t-test at $P < 0.05$) of the results found by the developed methodology. Good accuracy was achieved in different ranges of concentration of the analyte and iron.

Table 2 Results obtained for several interferent/analyte ratios as relative signals in comparison with 1.0 µg mL^{-1} Al(III) solution

Interferent/ analyte ratio	Fe(III)	Co(II)	Cu(II)	Zn(II)
20	1.00	1.01	1.00	1.00
50	1.00	1.01	1.01	1.01
100	1.00	1.12	1.12	1.03
150	1.01	1.21	1.15	1.24
200	1.19	1.32	1.21	1.29

Table 3 Results obtained in the analysis of some certified silicate and iron ore materials

Sample	Al$_2$O$_3$ certified[a] (%)	Al$_2$O$_3$ found by FIA-PUF method (%)	Fe content[a] (%)
JR-1 (Rhyolite)	12.89	13.3 ± 0.5	0.67
RGM-1 (Rhyolite)	13.72	14.0 ± 0.3	1.30
STM-1 (Syenite)	18.39	17.7 ± 0.2	3.65
AGV-1 (Andesite)	17.15	16.6 ± 0.5	4.74
BIR-1 (Basalt)	15.35	15.8 ± 0.4	7.88
IPT-27 (Iron ore)	1.76	1.74 ± 0.04	61.9
IPT-23A (Iron ore)	1.21	1.19 ± 0.04	65.8
IPT-21A (Iron ore)	0.75	0.79 ± 0.02	68.5

[a] Data from K. Govindaraju, *Geostand. Newsl.*, July 1994, **18**, Special Issue, and Instituto de Pesquisas Tecnológicas, São Paulo, Brazil.

5 Conclusions

Polyurethane foams have been used as solid sorbent for preconcentration and separation of metallic cations from thiocyanate medium in batch, column and on-line procedures. In this work, the flow injection system developed, using a minicolumn containing PUF, presents some important features such as very low overpressure, low cost and easy operation coupled to an enhancement of selectivity for spectrophotometric procedures. Also, the PUF under the experimental conditions did not show any swelling inside the minicolumn.

The proposed FIA system showed great selectivity by using PUF minicolumns, allowing the spectrophotometric determination of aluminum in low concentrations and in the presence of high amounts of interferent ions. Concentrations such as 170 µg mL^{-1} iron(III), 150 µg mL^{-1} manganese(II), 100 µg mL^{-1} zinc(II) and 50 µg mL^{-1} copper(II) and cobalt(II) can be tolerated when aluminum (1.0 µg mL^{-1}) is determined in the samples. The use of larger columns containing a greater amount of the solid sorbent can improve this selectivity with a small decrease in the analytical throughput. Achieved results showed that the proposed method had very good precision and accuracy when it was applied in the determination of aluminum in silicate and iron ore samples. Time required to clean the minicolumn (2 min) was the main factor for the moderate analytical throughput of the system.

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