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Exploiting multivariate calibration for compensation of iron interference in the spectrophotometric flow-based catalytic determination of molybdenum

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A B S T R A C T

Multivariate calibration involving partial least squares was exploited in the flow-based spectrophotometric determination of molybdenum in river waters relying on the Mo(VI)-catalyzed iodide oxidation by H_2O_2 under acidic conditions. Two sample aliquots were simultaneously inserted into the carrier stream, and differential pumping was accountable for in-line addition of sulfuric acid to one of them. Pronounced gradients (acidity and reagent concentrations) were established along the complex sample zone formed, and the absorbance-time function was characterized by local maximum and minimum values. As these values were intrinsically more precise, they were used for implementing the PLS multivariate calibration. Mo(VI) and Fe(III) were jointly determined, and Fe(III) interference was straightforwardly circumvented. Influence of reagent concentrations, acidity, available time for reaction development, and nature of the acid was investigated, and this later parameter manifested itself as relevant for discriminating purposes. The calibration set consisted of $6.2 – 50.0\ \mu g\ L^{-1}$ Mo(VI) plus $0.5 – 7.0\ mg\ L^{-1}$ Fe(III) solutions. The PLS model was characterized by good prediction ability [RMSEP = $0.67\ \mu g\ L^{-1}$ for Mo(VI)]. The innovation was applied to spiked river waters, and analytical precision, sampling rate, recovery, detection limit and reagent consumption were estimated as $0.5 – 2.4\%$, $31\ h^{-1}$, 98–114%. $0.88\ \mu g\ L^{-1}$ Mo(VI), and 54.0 mg KI per determination, respectively. Results were in agreement with ICP OES.

1. Introduction

The spectrophotometric method for molybdenum determination relying on the Mo(VI)-catalyzed oxidation of iodide by H_2O_2 under acidic conditions was proposed in 1956 by Yatsimirskii and Afanas'eva [1] who stressed its analytical sensitivity, simplicity and ruggedness, as well as the development of the chemical reactions under mild conditions. The method was automated by Hadjiioannou [2], who reported that presence of H_2SO_4 and HCl leads to similar results. Good selectivity in relation to metallic ions, as well as oxidizing, reducing and complexing agents was noted, and the positive interference of Fe(III) manifested itself for Fe/Mo concentration ratios higher than 32. The method was implemented in a segmented flow analyzer in 1970 [3] and, in 1983, was the first catalytic method carried out in a flow injection analyzer [4].

Iron has been often mentioned as a potential interfering species in the analysis of agro-environmental samples such as *e.g.* natural waters, plant tissues, soils and sediments [5], but there appear to be no reports on the role of Fe(III) in the indicator reaction. In order to circumvent the Fe(III) interference, different strategies involving hydrolysis,

masking, separation or joint determinations have been proposed. Hydrolysis of Fe(III) was accomplished by adjusting the pH (5 < pH < 9) aiming at the formation of slightly soluble iron oxides [4], but a previous filtration step was needed, making the procedure cumbersome.

Regarding masking, preliminary experiments revealed that Fe(III) complexation with fluoride [6] or EDTA was not effective for quantitatively suppressing the interference of $2.0\ mg\ L^{-1}$ Fe(III) in the determination of $20.0\ \mu g\ L^{-1}$ Mo(VI).

In-line separation by cation-exchange was effective for suppressing the Fe(III) interference in the analysis of plant digests [7], as the ferric cations were sorbed whereas the molybdate anions ideally passed through the resin mini-column without interaction. Good figures of merit were attained, but the authors reported that *ca.* 10% of the analyte was retained. In addition, the flow system was somewhat complex.

Circumventing the Fe(III) interference through flow-based joint determinations is also feasible. In the original procedure [5], the sample was handled twice, one of them involving sulfosalicylic acid addition by confluence. The formed iron(III) salicylate complex was monitored at 490 nm, allowing the determination of Fe(III), and the result was taken

into account to compensate the contribution of Fe(III) to the Mo(VI) analytical signal gathered at 350 nm. Good analytical figures of merit were attained in the analyses of plant and food digests with 2.0 − 100 µg L^{-1} Mo(VI) plus 0.6 − 25 mg L^{-1} Fe(III).

Joint determinations was also relevant in relation to the W(VI) interference. In this context, a flow-injection system analogous to that above mentioned [5] was proposed for molybdenum and tungsten determination in geological samples [8]. Two sample zones were sequentially established into the main carrier stream, and a citric acid zone was added to the first one by zone merging [9] in order to mask W(VI). The recorded peaks reflected then the Mo(VI) and the Mo(VI) + W(VI) concentrations. Good analytical figures of merit were attained, but a complex flow system was required. Analogously, these analytes were determined in alloys with high iron contents [10]. With differential pumping, two sample zones were established into the main carrier stream, one of them spiked with citric acid, and Fe(III) interference was circumvented though in-line ion-exchange. In a flow system with differential pumping, the pump is accountable for aspirating two merging streams (the sample and another solution to be added to it) and for pumping this solution [11]. The difference in flow rates determines therefore the sample aspiration rate. A noteworthy aspect is that the sample stream does not flow through the pump before the sampling step.

Joint determinations exploiting multicomponent analysis is another possibility, as foreseen by Lukkari and Lindberg [12], who emphasized the potentialities of partial least squares (PLS) calibration in continuous flow and flow-injection analysis. This possibility was demonstrated by Whitman et al. [13] in relation to first-order calibration methods such as classical least squares (CLS), principal component regression (PCR), and PLS. To this end, a single-line flow system was proposed for the spectrophotometric determinations of nickel and iron in plating bath solutions [14]. Nickel was monitored as the green aquo-complex, whereas iron was oxidized by persulfate and complexed with thiocyanate. The sample and reagent solutions were inserted into the same carrier stream, and the resulting zones penetrated each other during transportation towards detection, so that concentration gradients were established along the complex formed zone. Successive measurements gathered during sample passage through the flow-cell, permitted multivariate calibration strategies to be straightforwardly applied.

A noteworthy aspect of the above application is that every measurement is associated to a different fluid element, thus a different sample handling condition, meaning a given sample dilution degree, a reagent concentration and a mean residence time. One can imagine therefore a "pseudo-sensor" adherent to it [15]. This concept was coined in relation to the joint determinations of iron and vanadium in alloys [16] exploiting the catalytic effects of Fe(II) and V(IV) on the rate of iodide oxidation by Cr(VI) under acidic conditions. The Jones reductor was needed for analyte conversions to Fe(II) and V(IV). The sample was inserted into an acidic KI solution acting as sample carrier stream, a Cr(VI) reagent solution was added downstream by confluence, and successive measurements were gathered.

Further, limitations in system ruggedness related to the inherent low repeatability of measurements performed in sample regions with pronounced concentration gradients [17] were minimized by successively inserting three sample aliquots into the same carrier stream [15]. Overlap of the established zones yielded a complex sample zone with several regions of maximal and minimal absorbance values where concentration gradients were less pronounced, thus improving the measurement repeatability. The proposed system was very simple and rugged, yielding good analytical figures of merit.

The aim of this work was to propose a novel flow-based strategy involving differential pumping, measurements in regions with low concentration gradients and multivariate calibration in order to improve the catalytic determination of molybdenum in river waters through joint determinations. Molybdenum is an essential microelement present in natural waters, and its requirement for adults is about

25 µg per day. Over-ingestion may however result in the incidence of gout, disturb the Ca and P metabolism, osteoporosis and articular abnormity [18].

2. Experimental

2.1. Samples, standards, reagents

All solutions were prepared with chemicals of analytical-grade quality and deionized water (resistivity > 18.2 MΩ cm). Water samples from Jaguari, Ribeirao das Posses, Piracicaba and Camanducaia rivers (Brazil) were collected into 1000-mL polyethylene flasks, filtered through 0.45 µm acetate cellulose membrane filter, preserved with addition of 1.0 mL nitric acid (meaning 0.014 mol L^{-1} HNO_3) and kept under refrigeration (*ca.* 4 °C) [19].

The 100.0 mg L^{-1} Mo(VI) stock standard solution was prepared by dissolving ammonium heptamolybdate tetrahydrate in water, and the 1000 mg L^{-1} Fe(III) stock standard solution was based on iron(III) oxide [20]. Working standards were prepared in 0.014 mol L^{-1} HNO_3 and covered the 6.00 − 50.0 µg L^{-1} Mo(VI) or 0.50 − 7.00 mg L^{-1} Fe(III) ranges. Single element standard solutions were used for investigating the influence of the main involved parameters, whereas Mo(VI) + Fe(III) standards (Table 1) were used for PLS application.

The R_1 reagent (Fig. 1) was a 0.04% (w/w) H_2O_2 solution daily prepared by dilution of a titrimetrically standardized 30% (w/w) commercial stock, R_2 was a 3.5% (w/v) KI solution, and R_3 was a 0.15 mol L^{-1} H_2SO_4 solution.

2.2. Apparatus

The flow systems comprised a model USB 4000 Ocean Optics UV–vis spectrophotometer (Dunedin FL, USA); a model IPC-4-V2.00 Ismatec peristaltic pump (Wertheim, Germany) with Tygon pumping tubes; an injector-commuter [21]; sampling loops, coils and transmission lines built-up with 0.8 mm i.d. polyethylene tubing; and accessories. The spectrophotometer was furnished with P400-1 optical fibers, a HL-2000 halogen radiation source and a model 178.710-QS Hellma flow cell (Müllheim, Germany) with 80-µL inner volume and 10-mm optical path. The SpectraSuite software was accountable for data acquisition and treatment. In order to operate in the visible region, the wavelength was shifted from 353 to 410 nm, leading to a 30%-decrease in absorbance for both analytical and baseline measurements [6]. Sample monitoring involved a 16-ms integration time, and a smoothing relying on a 4-point moving average. The 4.0.2 PLS toolbox of the version 7.0 Matlab software was used for multivariate calibration.

2.3. Flow diagrams

The flow system in Fig. 1a was designed to investigate the influence of the main involved parameters, aiming at to improve the sensitivity in the Mo(VI) determination and to increase the Mo(VI)/Fe(III) analytical signal ratio through kinetic discrimination. In the situation specified in

Table 1
Standard solutions. STD: standard solutions for calibration; Mo(VI) and Fe(III) concentrations in µg L^{-1} and mg L^{-1}; * solutions for validation of the PLS model.

STD	Mo(VI)	Fe(III)	STD	Mo(VI)	Fe(III)	STD	Mo(VI)	Fe(III)
1	0.00	0.00	9	0.00	7.00	17	50.0	3.00
2	6.25	0.00	10	12.5	1.00	18	50.0	7.00
3	12.5	0.00	11	12.5	3.00	*19	20.0	2.00
4	25.0	0.00	12	12.5	7.00	*20	40.0	2.00
5	50.0	0.00	13	25.0	1.00	*21	30.0	4.00
6	0.00	0.50	14	25.0	3.00	*22	30.0	6.00
7	0.00	1.00	15	25.0	7.00	*23	45.0	3.5
8	0.00	3.00	16	50.0	1.00			