A rugged flow-based procedure for spectrophotometric determination of molybdenum in steel

Josiane M.T. Carneiro, Ana Cristi B. Dias, Elias A.G. Zagatto[*]

Centro de Energia Nuclear na Agricultura, Universidade de S Paulo
P.O. Box 96, Piracicaba SP 13400-970, Brazil

Abstract

The novel reagent 3,5-dibromo-4-hydroxyphenylflurone (DBHF) is exploited in order to design a rugged sequential injection procedure for spectrophotometric determination of molybdenum in steels. DBHF interacts with Mo(VI) under acidic conditions yielding a 1:2 reddish complex (λ_{max} = 530 nm). Beer's law is followed up to 100 mg l^{-1} Mo (r > 0.998; n = 5). Sensitivity and detection limit were estimated as 0.007 absorbance l mg^{-1} and 0.05 mg l^{-1} Mo, respectively, this latter value corresponding to 0.002 % (w/w) in the steel. Measurement frequency is 60 h^{-1}, and reagent consumption is 250 mg DBHF per determination. Results are precise (r.s.d. < 0.5 %) and in agreement with ICP-OES and with certified values of standard reference materials.

Keywords: flow analysis, spectrophotometry, molybdenum, steel, sequential injection system.

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1. Introduction

The availability of fast analytical procedures is essential for an efficient process control in the metallurgical industry, and *in situ* analysis is a good alternative for real-time control in the alloy manufacturing [1]. With an efficient and compact analyzer, as well as a suitable feedback mechanism, the amounts of the constituents within the molten batch are better defined and the quality of the final product is improved. Search for strategies to enhance versatility and speed of analysis, and to decrease the need for previous sample treatment has been unceasing [2]. This holds also for molybdenum that plays an important role in the steel making process, as it influences the alloy hardness and the resistance against temperature and corrosion [3,4].

To this end, flow analysis with spectrophotometric detection should be highlighted due to its characteristics of portability and robustness of the related instruments, besides other advantageous figures of merit. The number of flow-based analytical applications for process monitoring is then impressive [2,5,6], matching the present tendency towards enhancement of the automation level.

SIA systems [7] are very versatile, thus attractive in situations where system ruggedness is needed. Its suitability to process analysis has been often emphasized [8]. Sample and reagent aliquots are selected by the action of a single multi-port selecting valve, and sequentially aspirated towards a holding coil, establishing a reproducible sample zone. The flow is then reversed and the zone is transported towards detection. Potentialities, limitations and application range of this system have been already discussed [8,9]. A noteworthy feature of SIA is the feasibility of setting the involved parameters such as *e.g.* flow rates, sample and reagent aliquots, speed of analysis, and aspiration sequence of the involved solutions, without modifying the system architecture. System optimisation can thus be in-line performed.

The aim of this work was to develop a SIA system for spectrophotometric determination of molybdenum in steel using the recently proposed [10] 3,5-dibromo-4-hydroxylphenyl-flurone (DBHF) as colour-forming reagent. System ruggedness is aimed. The method involves complex formation (1 mol Mo^{6+} to 2 mol DBHF) under acidic conditions, and maximum absorption is noted at 530 nm.

The need for such a procedure is justified by recalling that spectrophotometric determination of molybdenum in steels generally exploits complexation [11,12] or catalysed oxidation [13,14]. The former is usually based on reaction with thiocyanate that requires addition of a large amount of tin chloride and very high acidic conditions [12,15,16]; moreover, toxic products are formed and this is against the tendency towards a clean chemistry [17]. The latter generally exploits the influence of Mo^{6+} on the rate of oxidation of iodide by hydrogen peroxide under mild conditions [13]. Best results are obtained at pH 1.6 [14,18,19] that is not easily maintained in view of the lack of a suitable buffer system [20]. Moreover, the procedure is very sensitive; therefore a preliminary step of sample dilution is usually required.

2. Experimental

2.1. Samples, standards, reagents

All solutions were prepared with analytical-quality reagents. DBHF was synthesized as described elsewhere [10].

The steel samples were drilled and the resulting fillings were sieved (1.19 sieve), washed with 0.01 mol l^{-1} HNO_3, and dried. About 250 mg of fillings were placed inside digestion tubes, 10 ml of *aqua regia* (HNO_3 : HCl :: 3 : 1, v/v) were added, and the tubes were placed in a digester block. The temperature was set as 100 ^{o}C and maintained during about 15 min for complete sample dissolution. The vapour phase was allowed to condense and recycle. After cooling the digester block to room temperature, the sample volumes were filled up to 100 ml with water [12].

The stock standard solution (1000.0 mg l^{-1} Mo) was monthly prepared by dissolving 460.0 mg $(NH_4)_6Mo_7O_{24}.4H_2O$ in about 200 ml of water, adding 5.0 ml of 5.0 mol l^{-1} HNO_3 and completing the volume to 250 ml with water. Working standards (10.0 - 100.0 mg l^{-1} Mo) were weekly prepared by diluting the above stock solution with water-diluted (1:9 v/v) *aqua regia*.

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* Corresponding author: E-mail: ezagatto@cena.usp.br

The R_1 reagent (Fig. 1) was prepared by adding 0.08 g DBHF, 10 ml of 6.0 % (w/v) Triton X-100 and 50 ml of 96 % (v/v) ethanol to a 100-ml flask and filling the volume up to mark with water. The R_2 reagent was a 3.0 mol l^{-1} H_3PO_4 solution, also 0.2 mol l^{-1} $P_2O_7^{2-}$ (as sodium salt). The C carrier stream was a water-diluted (1:9 v/v) *aqua regia* solution; as this solution presented similar matrix as the samples, establishment of undesirable concentration gradients along the sample zone, which could impair detection, was minimized.
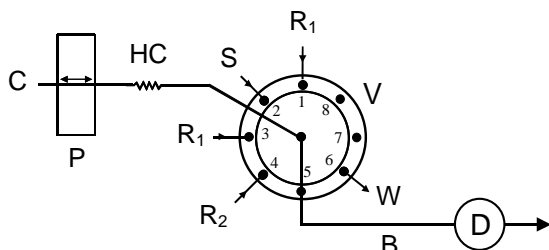

Fig. 1. Flow diagram. S = sample (0.0 – 100.0 mg l^{-1} Mo); C = carrier stream (water diluted *aqua regia*); R_1 = colour forming reagent (0.08 % w/v DBHF + 0.6 % v/v Triton X-100 + 48 % v/v ethanol); R_2 = masking reagent (3.0 mol l^{-1} H_3PO_4 + 0.2 mol l^{-1} $2O_7^{2-}$; P = peristaltic pump; HC = holding coil (*ca* 400 cm); B = transmission line (80 cm); V = selecting valve; D = detector (530 nm); W = waste collector.

For obtaining selectivity data, 10.0 and 75.0 mg l^{-1} Mo solutions were prepared each one with a different concentration of a potential interfering species (100 mg l^{-1} Cu^{2+}, Si^{4+}, Mn^{2+}, V^{3+} or W^{6+}; 250 mg l^{-1} Cr^{3+}; 500 mg l^{-1} Ni^{2+}, Co^{2+} or Al^{3+}, 1000 mg l^{-1} Fe^{3+}, as Cu^0, $Na_2SiO_3 \cdot 5H_2O$, MnO_2, V_2O_5, $Na_2WO_4 \cdot 2H_2O$, $CrCl_3 \cdot 6H_2O$, Ni^0, $CoSO_4 \cdot 7H_2O$, Al-Titrisol – Merck, and Fe_2O_3, respectively). These concentrations are beyond the expected ones, considering their typical constitution of the steel alloys [3] and the procedure for sample dissolution.

2.2. Apparatus

The SIA system comprises a model IPC-4 Ismatec peristaltic pump with a 0.4-mm i.d. Tygon pumping tube, a model E8 Valco eight-port selecting valve, a model 432 Femto spectrophotometer with a model 178-OS Hellma flow cell (80-µl inner volume, 10-mm optical path) and accessories. Whenever needed, a model 111 Kipp & Zonen strip-chart recorder was also used. The peristaltic pump and the selecting valve are controlled by a Pentium II microcomputer (interface card: Advantech PCL-711; language: Quick Basic 4.5). The manifold is built-up with 0.8-mm i.d. polyethylene tubing of the non-collapsible wall type.

2.3. Procedure

Considering the expected analyte contents in the injectate and the inherent sensitivity of the method [10], the flow system was designed to provide large sample dispersion [21]. The ports of the selecting valve were defined to minimize the time interval needed for valve switching among the different positions. Time intervals and flow-rates for solution aspiration / propelling were selected aiming simplification of the system operation. The transmission line between the selecting valve and detector was kept as 80 cm. In relation to the washing steps (Tab. 1) high flow rates were set in order to improve sampling rate and to attain a more stable baseline. The volumes of sample and reagents were

selected as a compromise with analytical sensitivity, mixing conditions (peak smoothness) and measurement repeatability.

System operation is summarized in Table 1. The selected aliquots were directed towards the HC holding coil that was attached to the valve central port (Fig. 1). Six of the eight ports available in the valve were used, but only one of them was linked with the central port at a time.

Tab. 1. Operating conditions. Table refers to the SIA system in Fig. 1. S = sample; C = carrier stream; HC = holding coil; R_1 and R_2 = reagents.

Step	Operation	Port	Time (s)	Flow rate (ml min^{-1})
1	R_1 aspiration towards HC	1	2	1.90
2	S aspiration towards HC	2	2	0.16
3	R_1 aspiration towards HC	1	2	1.90
4	R_2 aspiration towards HC	4	2	2.70
5	C propelling towards the detector	5	60	2.70

Before analysis, the S, R_1 and R_2 solutions were sequentially aspirated towards HC and propelled towards detection in order to fill the corresponding sampling channels thus allowing initialisation of the analytical cycle. The carrier stream was then aspirated towards HC and pumped towards waste in order to wash the analytical path. Thereafter, the sample and involved reagents were aspirated towards HC according to the $R_1/S/R_1/R_2$ sequence (steps 1 - 4). Rotation of the peristaltic pump was then reversed, and the established sample zone was pushed towards the flow through detector (step 5). Passage of the sample though it resulted in a transient variation in the monitored absorbance (530 nm) recorded as a peak proportional to the molybdenum content in the sample.

The main involved parameters were studied by handling the standard solutions in triplicate into the system outlined in Fig. 1. Whenever required, standard solutions with a potential interfering species were also handled.

Aspiration sequence and selected volumes of the involved solutions were investigated by modifying the system operating conditions (Table 1) via keyboard. The reagent concentrations were investigated within the 0.02 - 0.1 % (w/v) DBHF, 0.1 – 5.0 mol l^{-1} H_3PO_4 and 0.0 – 0.5 mol l^{-1} $P_2O_7^{2-}$ ranges. Sample acidity was investigated within 0.1 – 1.0 mol l^{-1} H^+ by using standard solutions prepared with different water-diluted *aqua regia*. The proportion HNO_3:HCl was maintained as 3:1 (v/v) in order to simulate the different dilutions of the *aqua regia*. Temperature was investigated within 10 and 60 °C by immersing the S, C, R_1 and R_2 bottles, as well as the holding coil in a thermostatic water bath.

After system dimensioning, the main figures of merit were evaluated. Precision was estimated after 6-fold repetitive analyses of typical samples. Analysing standard reference materials and/or samples already run by ICP-OES [22] assessed accuracy. Thereafter, the system was applied to routine large-scale analysis.

3. Results and Discussion

The aspiration sequence of the involved solutions is a relevant aspect to be taken into account for system design, and was defined as $R_1/S/R_1/R_2$ (Tab. 1). Distortions in recorded peak and limitations in sensitivity were observed when too low R_1 volumes (< 60 µl) were inserted. Increasing this volume from 60 to 200 µl improved sensitivity, but the recorded peaks were less smooth, reflecting deterioration in the mixing conditions; moreover double peaks manifested themselves especially in

relation to lower Mo concentrations. It was then decided to insert two R_1 reagent aliquots of 60 µl, before and after the sample. Better interaction of the analyte with DHBF was then attained as improved repeatability (r.s.d. < 2 %) was noted under all the investigated situations. An additional factor leading to the improvement of the mixing conditions of these three aliquots is the flow reversal inherent to the sequential injection system. With a very low sample volume (5 µl) double peaked recording was not noted, as overlap between both reagent zones was efficiently attained.

The R_2 aliquot should be added as the last one as its interaction with the sample is not a limiting factor. Its positioning between the other aliquots led always to the appearance of double peaks reflecting the limitations in the Mo^{6+} – DBHF interaction. Addition of the colour-forming reagent before the masking agent is not usual in spectrophotometric procedures. In this present situation, this was not a limiting factor, as chemical equilibrium was more relevant relatively to reaction kinetics.

Regarding reagent concentrations, increasing the DBHF concentration in R_1 within 0.04 and 0.08 % (w/v) improved the analytical sensitivity (Fig. 2). However, a pronounced increase in baseline was observed beyond 0.08 % (w/v) decreasing the signal-to-noise ratio. This concentration was then selected.
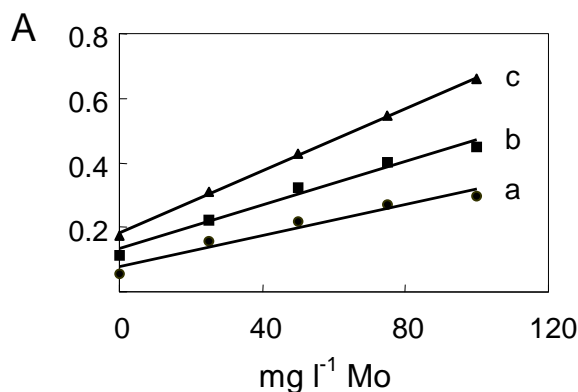

Fig. 2. Influence of reagent concentration. Curves a, b and c correspond to 0.04, 0.06 and 0.08 % (w/v) DBHF.

Increasing H_3PO_4 concentration within 1.0 and 5.0 mol l^{-1} caused slightly lessening in sensitivity (< 5 %). For higher concentrations, the decrease in sensitivity was more pronounced and schliere noise was noted. On the other hand, a lessening in the masking efficiency in relation to Fe^{3+} was noted for < 1.0 mol l^{-1}. These observations are in agreement with recent information [22]. With 3.0 mol l^{-1} H_3PO_4, interference from Fe^{3+} was quantitatively circumvented and the decrease in analytical signal relatively to 1.0 mol l^{-1} H_3PO_4 was only of about 10 %. Moreover, the system presented good buffer capacity. In fact no influence was noted when sample acidity was varied within 0.1 and 0.5 mol l^{-1} H^+ (water diluted *aqua regia*).

Amongst the investigated potential interfering chemical species, significant interferences were observed only for Fe^{3+} and Cr^{3+}, the former one being quantitatively masked with phosphoric acid. Pyrophospate was efficient for Cr^{3+} masking, and its concentration was selected as 0.2 mol l^{-1}.

Regarding temperature, no influence was observed when it was varied within 10 and 60 °C. Considering the system ruggedness, it was decided to operate it at *ca* 25 °C, maintained through air conditioning facilities.

The proposed system is very rugged, as it is only slightly affected by variations of the main involved parameters. Consequently, negligible modifications in the coefficients of the analytical curve were observed during 4-h operating periods, and a stable baseline was always noted. The sample undergoes high in-line dilution, the volumetric fraction being estimated as 0.014 by taking advantage of the dye approach [21]. Matrix affects become then less relevant, and this is a beneficial aspect regarding system ruggedness.

The analytical curve is linear (r > 0.99976; n = 6), and peak heights of about 0.7 absorbance correspond to 100.0 mg l^{-1} Mo. The analytical frequency is 60 h^{-1}, and the reagent consumption is 250 µg DBHF per determination. Detection limit was estimated as 0.05 mg l^{-1} Mo that corresponds to 0.002 % (w/w) in the steel. Results are precise (r.s.d. < 0.5 %) and in agreement with certified values of standard reference materials and with results obtained by ICP-OES (Table 2). Statistical differences between data sets were not confirmed after applying the Student's *t*-test at the 95 % confidence level ($t_{exp} = 0.195 < t_{tab} = 2.365$).

Tab. 2. Results. Molybdenum contents determined by ICP-OES [21] and by the proposed procedure (SIA). Numbers between brackets = estimates of uncertainties, in %, based on six replications. Standard reference materials with indication of Mo certified values (SRM) from AISI (American Iron and Steel Institute), ASTM (American Society for Testing and Materials) and IPT (Instituto de Pesquisas Tecnológicas, Brazil); 1 – 3 = typical samples.

Sample	Main constituents, % w/w	Mo content, % w/w		
		SRM	ICP-OES	SIA
AISI 316L-A	0.20 Si, 1.81 Mn, 10.72 Ni, 17.38 Cr, 0.016 C	2.26	-	2.27 (0.8)
ASTM F-138	0.22 Si, 1.81 Mn, 13.86 Ni, 17.60 Cr, 0.41 Cu, 0.018 C	3.08	-	3.05 (1.0)
ASTM 316L-B	0.31 Si, 1.65 Mn, 8.04 Ni, 18.02 Cr, 0.074 C	1.01	-	1.09 (1.2)
IPT 75	2.0 Si, 0.72 Mn, 0.432 Cu, 0.431 Ni, 0.487 Cr, 0.023 Ti, 0.032 V	0.439	-	0.44 (0.9)
IPT 29A	0.372 Si, 0.565 Mn, 0.012 Cu, 0.794 Ni, 0.845 Cr, 0.028 Al, 0.008 V	0.276	-	0.28 (1.3)
1	0.42 Si, 1.26 Mn, 10.70 Ni, 16.42 Cr, 0.027 C	-	2.22 (0.7)	2.27 (0.9)
2	0.48 Si, 1.24 Mn, 10.52 Ni, 16.19 Cr, 0.027 C	-	2.13 (0.9)	2.07 (0.8)
3	0.57 Si, 1.26 Mn, 10.80 Ni, 16.61 Cr, 0.027 C	-	2.23 (1.1)	2.20 (0.9)

4. Conclusions

The proposed system is suitable for steel analyses. Synthesis of DBHF is not cumbersome; anyhow, one expects the sooner commercial availability of this reagent. No sample dilution other than that inherent to the dissolution step is required. As the required reagent volume is very low, waste generation is minimal. Moreover, the proposed system yields fast results and is easily transported. These characteristics of ruggedness and portability are positive factors towards system application to *in situ* analysis. Studies regarding this aspect are presently in progress.

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