

# Determination of Tin, Vanadium, Iron, and Molybdenum in Various Matrices by Atomic Absorption Spectrometry Using a Simultaneous Liquid–Liquid Extraction Procedure

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## Abstract

An atomic-absorption spectrometric method is described for the determination of tin, vanadium, iron, and molybdenum in two certified reference materials, food samples, and petroleum crude. After treatment with acids, these elements are separated from matrix elements by simultaneous solvent extraction of 5,5'-methylenedisalicylohydroxamic acid complexes from HCl/NaClO<sub>4</sub> solution into an isobutyl methyl ketone/tributyl phosphate solution. The detection limits range from 0.018 to 0.19 µg/mL (*n* = 3), and the relative standard deviations do not exceed 2.0% at levels of 0.5, 0.6, 2.0, and 7.0 µg/mL of Fe, Mo, V, and Sn, respectively. The method is selective and suffers only from interference by Zr(IV), Ti(IV), Th(IV), W(VI), PO<sub>4</sub><sup>3-</sup>, and F<sup>-</sup>.

## Introduction

Among the many metals found in the body, only a small number are known to be essential for normal life. The absence of these metals will result in the appearance of characteristic pathological deficiency symptoms. Iron (Fe), molybdenum (Mo), and tin (Sn) are considered micronutrient metals essential for body function, whereas vanadium (V) has not been established as essential, although there is evidence of its involvement in some cell reactions. It is not always possible to draw a distinction between essential and toxic metals, probably because all metals are potentially toxic if ingested in sufficient amounts (1,2). Foods may contain elevated amounts of Fe and Sn because of leaching of the metals from the container walls. In like manner, considerably higher than average levels of Mo can occur in herbage and vegetables in areas where the soil is naturally enriched with the metal, Mo-containing fertilizers are used, or industrial pollution occurs. On the other hand, it is known that seafood contamination by petroleum crudes,

which contain V in the form of porphyrin complexes, can be checked by determining the levels in vanadium.

All in all, it is useful to develop analytical methods that permit the determination of several elements with a minimum effort. In this respect, the use of a group of ligands in liquid–liquid extraction allows various metal species to be separated from the other components in a sample in a single step. If this procedure is followed by the use of a selective measurement technique such as an atomic spectroscopy or a chromatographic technique, the species can be determined simultaneously, taking advantage of the same extraction process. Group ligands include such well-known reagents as dithizone (3), diethyldithiocarbamate (DDC) (4), or 8-hydroxyquinoline and its derivatives (5), although there are a few cases in which multi-elemental extraction has been combined with the absorption spectrophotometric (AAS) determination of the extracted ions. Application of 5,5'-methylene-disalicylohydroxamic acid (MEDSHA) to the AAS determination of Sn (6), V (7), Mo (8), and Fe (9) has been described previously. On the other hand, we have found that there are specific experimental conditions that allow the simultaneous solvent extraction of these metal ions (10). On the basis of these facts, we developed in this work a method for the determination of these four elements by AAS. The proposed method, which has few interferants, was applied to the analysis of several food samples, a river sediment, and a petroleum crude with good results.

## Experimental

### Apparatus

A Perkin-Elmer (Norwalk, CT) model 2380 atomic absorption spectrophotometer was used with the following operating conditions: wavelength: 318.4 nm for V, 248.3 nm for Fe, 313.3 nm for Mo, and 286.3 nm for Sn; lamp current: 35 mA for V, 30 mA for Fe and Sn, and 25 mA for Mo; slit width: 0.7 nm for V, 0.2 nm for Fe, 0.7 nm for Mo, and 0.7 nm for Sn. For V, Mo, and Sn,

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the dinitrogen oxide/acetylene ratio and the burner position were adjusted for maximum sensitivity. For Fe, the flame was air/acetylene.

All pH measurements were made with a Crison (Alella, Barcelona, Spain) micropH 2000 pHmeter equipped with a combined calomel-glass electrode assembly. The Statgraphics statistical software package was used for data manipulation.

### Reagents

Stock standard solutions of 1000 µg/mL for each metal were prepared from analytical-grade reagents (Merck, Darmstadt, Germany) and used for further dilutions. The synthesis of MEDSHA has been reported previously (11). Solutions of this reagent were prepared in dilute ammonia. Ultrapure water was obtained from a Milli-Q RO 12 PLUS water system (Millipore Corp., Bedford, MA). All other reagents and organic solvents used were of analytical reagent grade.

### Procedure

A measured sample, containing less than 100 µg of V, 25 µg of Fe, 30 µg of Mo, and 350 µg of Sn, was transferred into a 250-mL separating funnel. Then the pH was adjusted to 2 with 0.25M HCl solution, and 3.3 mL of 5M NaClO<sub>4</sub> solution, 6.4 mL of 0.05M MEDSHA solution, and distilled water were added to obtain a final volume of 50 mL. The resulting solution was shaken for 2 min with 10 mL of 1.00M TBP solution in IBMK, and the organic phase was centrifuged and aspirated into the flame. A blank was prepared in the same fashion.

### Preparation of sample solutions

The food samples (oyster tissue (SRM 1566), spanish lentils, rice, and clam tissue) and the sediment sample (CRM N27-04) were dried at 110°C until they were of constant weight and ground into a fine powder, if necessary. The appropriate quantity of each sample was treated with HNO<sub>3</sub> in a sand bath (approximately 25 mL of acid for 5 g of sample), adding more nitric acid as necessary until foaming ceased. Ten milliliters of HClO<sub>4</sub> (70%, w/w) was then added, and the solution was evaporated to dryness. This process was performed twice. The residue was treated with 0.25M HCl solution to boiling, cooled, and filtered (Whatman no. 40 paper) and the solution was finally diluted to a known volume.

If a sample contained Sn, the treatment with HClO<sub>4</sub> had to be avoided in order to preclude the precipitation of this ion as H<sub>2</sub>SnO<sub>3</sub>. In that case, after the HNO<sub>3</sub> treatment, the solution was concentrated to 5–6 mL and heated with concentrated HCl until total elimination of HNO<sub>3</sub> was achieved. Finally, the solution was heated gently to reduce the volume to 2 mL and diluted to volume with distilled water.

The petroleum crude sample was treated with concentrated sulfuric acid with continuous agitation to avoid foam formation, followed by combustion of carbonaceous ash at 525 ± 25°C. The inorganic residues were digested for 10–15 min with hydrochloric acid (1:1). After concentration, a few drops of nitric and sulfuric acid were added; the solution was heated gently until

white fumes were formed and the small carbonaceous residue that had not been ignited was destroyed. The solution was finally diluted to a known volume.

## Results and Discussion

### Simultaneous solvent-extraction conditions

In a previous paper (10), we used a Doehlert design to optimize the experimental variables implied in the simultaneous extraction of Fe, V, Mo, and Sn as 5,5'-methylenebis(cyclohydroxamates). We found that the optimum conditions for the quantitative extraction of these ions were as follows: pH = 2.0 (HCl), [NaClO<sub>4</sub>] = 0.33M, [MEDSHA]<sub>a</sub> = 6.4mM, and [TBP]<sub>o</sub> = 1.0M, with a shaking time of 2 min and a phase-volume ratio of 5:1 (V<sub>a</sub>/V<sub>o</sub>).

### Calibration graph

The data were collected by well-designed experiments (using triplicate responses at each concentration and randomized arrangements). Tests for nonlinearity (for univariate linear calibration) were based on the analysis of the residual variance from a regression into parts owing to "lack of fit" and "pure error"; under these requirements the performance characteristics of the method, for each of the four ions, are given in Table I. The detection limits were calculated from the calibration data, following the criterion proposed by Sarabia et al. (12), which takes into account the statistics implied in the difference between the analytical signal and the blank signal, and also the variability produced for the presence of errors in the slope and in the intercept of the calibration graph. According to IUPAC recommendations, we assumed that there is a true and false positive of 0.05 (α = β = 0.05).

### Effect of foreign ions

A detailed study of interferences was made for cations and anions in amounts ranging up to 50 mg with 50.0 µg of V, 12.5 µg of Fe, 15 µg of Mo, and 100 µg of Sn. Ions were not considered as interfering if the mean value of three replicates produced an error in absorbance of less than 5%.

There was no interference from the following ions: Cs(I), Rb(I), Li(I), Tl(III), Ag(I), Zn(II), Ca(II), Co(II), Mg(II), Ba(II), Be(II), Ni(II), Mn(II), Pb(II), Sr(II), Cu(II), Cd(II), Hg(II), Pd(II),

**Table I. Performance Characteristics**

	Fe	Mo	V	Sn	
Linear range (µg/mL)	0.06–0.50	0.10–0.60	0.13–2.00	0.13–7	
Linearity (%)	99.0	98.2	99.4	99.2	
Sensitivity (µg/mL)	0.008	0.014	0.018	0.085	
Detection limit (µg/mL)	<i>n</i> * = 3 <i>n</i> = 10	0.018 0.012	0.030 0.020	0.040 0.030	0.19 0.130
RSD (c) <sup>†</sup> (%)	5.4 (0.1) 1.2 (0.5)	4.7 (0.2) 1.8 (0.6)	3.0 (0.4) 0.7 (2.0)	4.0 (1.4) 0.9 (7.0)	

\* *n* = number of determinations.  
<sup>†</sup> Relative standard deviation of the concentration (for *n* = 3) (Values in parentheses are in µg/mL).

Sb(III), As(V), Al(III), Cr(III), Y(III), La(III), In(III), Ce(III), UO<sub>2</sub>(II), I<sup>-</sup>, SCN<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Br<sup>-</sup>, citrate, in at least 500-fold mass ratio to each one of the analytes. Some of these ions, such as Ca(II), Ba(II), Be(II), Sr(II), Al(III), La(III), UO<sub>2</sub>(II), BO<sub>2</sub><sup>-</sup>, and SCN<sup>-</sup>, are partly co-extracted and must be back-extracted by shaking the organic phase with a new aqueous solution of pH 2 and 0.33M in ClO<sub>4</sub><sup>-</sup>. In the same way, I<sup>-</sup> and SCN<sup>-</sup> are masked in the presence of 1 g/L of Hg(II). Zr(IV), Ti(IV), Th(IV), W(VI), PO<sub>4</sub><sup>3-</sup>, and F<sup>-</sup> have low tolerance limits: PO<sub>4</sub><sup>3-</sup> and F<sup>-</sup> interfere only in relation with Sn, whereas the others react with MEDSHA to give bulky precipitates that adsorb the complexes of V, Fe, Sn, and Mo.

### Sample analysis

To check the applicability of the proposed method, the fol-

lowing samples, which contained two or more of the four metal ions, were analyzed: two reference material (RM) samples, oyster tissue (SRM 1566) and Buffalo River sediment (CRM, N27-04), and five noncertified materials, a petroleum crude for Fe and V, a Spanish lentil sample for Fe and Mo, a clam tissue for Fe and V, and two different rice samples that were spiked with V and Mo (rice 1) and Sn (rice 2) because they only contained iron.

First of all, it was necessary to know if there was a matrix effect in order to obtain bias-free analytical results. When the samples analyzed were not standard reference materials, a validation study was carried out on the basis of different calibration procedures.

*In the absence of a matrix effect.* We followed the statistic protocol proposed by Cuadros et al. (13), which was based on three calibration procedures (i.e., standard calibration [SC],

**Table II. Statistics for the Analysis of Fe, Mo, V, and Sn in Several Samples**

Samples	Element	Matrix effect	Youden blank	Significant difference between the slopes?		Accuracy test
				SC and AC	AC1 and AC2	
Oyster tissue (SRM 1566)	Fe	No	Yes	No	—	$t_{cal} = 1.018 < t_{crit} = 2.776$ ( $\alpha = 0.05$ , Df = 5) No significant difference
	V	No	No	No	—	$t_{cal} = 1.731 < t_{crit} = 2.776$ ( $\alpha = 0.05$ , Df = 5) No significant difference
Buffalo river sediment (CRM, N27-04)	Fe	No	No	No	—	$t_{cal} = 1.381 < t_{crit} = 2.776$ ( $\alpha = 0.05$ , Df = 5) No significant difference
	V	No	No	No	—	$t_{cal} = 2.496 < t_{crit} = 2.776$ ( $\alpha = 0.05$ , Df = 5) No significant difference
Spanish lentils ( <i>Herbun nonatum</i> )	Fe	No	Yes	No	—	$t_{cal} = 1.856 < t_{crit} = 2.365$ ( $\alpha = 0.05$ , Df = 7) No significant difference
	Mo	No	Yes	No	—	$t_{cal} = 0.055 < t_{crit} = 2.447$ ( $\alpha = 0.05$ , Df = 6) No significant difference
Clam tissue ( <i>Cititerea s.p.</i> )	Fe	No	Yes	No	—	$t_{cal} = 1.155 < t_{crit} = 2.447$ ( $\alpha = 0.05$ , Df = 6) No significant difference
	V	No	No	No	—	$t_{cal} = 1.076 < t_{crit} = 2.447$ ( $\alpha = 0.05$ , Df = 6) No significant difference
Light Arabia	Fe	No	No	No	—	$t_{cal} = 0.246 < t_{crit} = 2.365$ ( $\alpha = 0.05$ , Df = 7) No significant difference
	V	No	No	No	—	$t_{cal} = 0.743 < t_{crit} = 2.365$ ( $\alpha = 0.05$ , Df = 7) No significant difference
Rice 1	Fe	No	No	No	—	$t_{cal} = 0.715 < t_{crit} = 2.365$ ( $\alpha = 0.05$ , Df = 7) No significant difference
	V*	No	No	No	—	$t_{cal} = 1.181 < t_{crit} = 2.365$ ( $\alpha = 0.05$ , Df = 7) No significant difference
	Mo*	No	No	No	—	$t_{cal} = 1.690 < t_{crit} = 2.365$ ( $\alpha = 0.05$ , Df = 7) No significant difference
Rice 2	Fe	No	Yes	No	—	$t_{cal} = 0.042 < t_{crit} = 2.365$ ( $\alpha = 0.05$ , Df = 7) No significant difference
	Sn*	Yes <sup>†</sup>	No	Yes	No	$t_{cal} = 3.053 < t_{crit} = 4.032$ ( $\alpha = 0.01$ , Df = 5) No significant difference

\* Added to the sample before treatment.

† Saturated matrix/analyte interaction.

standard-additions calibration [AC], and Youden calibration [YC]). The slope, the intercept, and the standard deviation of regression of each of the calibration graphs were calculated.

First, the slopes of the lines obtained by SC and AC calibrations are compared using the *t*-test. Then it is determined if the intercepts of SC and YC regression lines differed significantly from each other, which would indicate that a systematic error due to matrix components is present. In that case, the true blank of the sample, known as the Youden blank, is determined as the difference between both intercepts.

Finally, the accuracy of the results is tested by comparing the analyte contents from the SC and AC graphs, using a *t*-test for the comparison of the two means. If the difference is not significant, it is concluded that the method is accurate, at least, in relation with the sample analyzed.

*In the presence of a matrix effect.* In this case, by applying the standards-addition methodology (AC), it is necessary that the proportional interactive effect does not change with the matrix-to-analyte ratio (14,15). This independence is evident from the observed linearity in the AC plot (15), provided that the spike range is sufficiently large. An alternative way of showing the presence of a matrix effect consists of trying out two AC calibrations at different sample levels (16). This approach, based on four calibration procedures, SC, AC<sub>1</sub> (sample level 1), AC<sub>2</sub> (sample level 2), and YC, uses the statistical methodology to verify the accuracy of the analytical results in the presence of corrigible systematic errors because it permits the detection of

constant and proportional errors. The constant component of the error (Youden blank) is determined from the data set obtained in the YC with different sample levels. An analysis of covariance applied to SC, AC<sub>1</sub>, and AC<sub>2</sub> and a comparison of the correspondent slopes permit detection of the presence of any matrix-analyte interaction. Thus, we conclude that at the sample level studied, there is a systematic error (a saturated matrix-analyte interaction) if the slopes of SC and AC<sub>1</sub> and SC and AC<sub>2</sub> are different and the slopes of AC<sub>1</sub> and AC<sub>2</sub> are statistically equal.

In order to obviate this systematic error, the analyte concentration in the measurement solutions,  $c_x(A_i)$ , is then calculated as the ratio of the difference between the corrected intercept of AC<sub>i</sub> ( $i = 1$  and  $2$ ) -  $a_Y$  (intercept of the Youden calibration) and the pooled slope of calibrations AC<sub>1</sub> and AC<sub>2</sub>.

Finally, the analyte concentration in the original sample,  $C_i$ , is calculated and the accuracy of the results obtained is evaluated with a *t*-test for  $[n(AC_1) + n(AC_2) - 3]$  degrees of freedom (16).

When the samples analyzed were RMs, the presence of a matrix effect was checked as described, and the accuracy of the results was established by a comparison of the experimental mean with the certified value ( $\alpha = 0.05$ ,  $n = 6$ ).

The results obtained in the analysis of the samples mentioned are summarized in Table II, where it can be observed that there is a saturated matrix-analyte interaction in the determination of Sn in the rice 2 sample. In all the cases, the accuracy

**Table III. Determination of Fe, Mo, V, and Sn in Several Samples**

Samples	Element	Proposed method				Other method or certified value (µg/g)
		Added (µg/g)	Found (µg/g)	Recovery (%)	RSD (%)	
Oyster tissue (SRM 1566)	Fe	—	194	—	1.24 ( $n = 6$ )	195*
	V	—	2.2	—	6.43 ( $n = 6$ )	2.30*
Buffalo river sediment (CRM, N27-04)	Fe	—	4.2	—	3.8 ( $n = 6$ )	4.11*
	V	—	92	—	3.2 ( $n = 6$ )	95*
Spanish lentils ( <i>Herbium nonatum</i> )	Fe	—	61	—	5.42 ( $n = 7$ )	62.12 <sup>†</sup>
	Mo	—	45	—	4.88 ( $n = 7$ )	41.09 <sup>‡</sup>
Clam tissue ( <i>Citorea s.p.</i> )	Fe	—	497	—	3.99 ( $n = 6$ )	500 <sup>†</sup>
	V	—	2.23	—	4.07 ( $n = 6$ )	2.26 <sup>§</sup>
Light Arabia	Fe	—	1.75	—	3.90 ( $n = 4$ )	1.69 <sup>†</sup>
	V	—	15.9	—	2.20 ( $n = 4$ )	16.3 <sup>  </sup>
Rice 1	Fe	—	6.0	—	9.00 ( $n = 5$ )	5.93 <sup>†</sup>
	V	2.50	2.5	101.3	9.08 ( $n = 3$ )	—
	Mo	6.00	6.2	102.8	6.77 ( $n = 4$ )	—
Rice 2	Fe	—	44.6	—	0.73 ( $n = 3$ )	45.1 <sup>†</sup>
	Sn	50.00	48.9	97.88	0.68 ( $n = 3$ )	—

\* Certified values.

<sup>†</sup> Determined by spectrometry using bathofenantroline disulfonic acid disodium salt (reference 17).

<sup>‡</sup> See reference 18.

<sup>§</sup> See reference 7.

<sup>||</sup> ASTM method (reference 19).

test indicates that the method is reliable, at least, for the samples analyzed. This is confirmed by the good agreement between our results and the certified values, or those obtained by other methods, and also by the recovery values (rice samples) shown in Table III. Likewise, the RSD values indicate a satisfactory precision.

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