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Catalytic adsorptive stripping voltammetry determination of ultra trace amount of molybdenum using factorial design for optimization

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Abstract

A highly sensitive procedure is presented for the determination of ultra-trace concentration of molybdenum by catalytic adsorptive stripping voltammetry. The method is based on adsorptive accumulation of the molybdenum (Mo)-pyrocatechol violet (PCV) complex on to a hanging mercury drop electrode, followed by reduction of the adsorbed species by voltammetric scan using differential pulse modulation. The reduction current is enhanced catalytically by chlorate. The influence of variables was completely studied by factorial design analysis. Optimum analytical conditions for the determination of molybdenum were established. Molybdenum can be determined in the range 1.0×10^{-3}–100.0 ng ml^{-1} with a limit of detection of 0.2 pg ml^{-1}. The influence of potential interfering ions on the determination of molybdenum was studied. The procedure was applied to the determination of molybdenum in mineral water and some analytical grade substances with satisfactory results.

Keywords: Catalytic adsorptive stripping voltammetry; Molybdenum; Factorial design optimization

1. Introduction

Molybdenum is a biologically essential trace element. This element plays an important role in a wide variety of plants, animals and alloys [1,2].

In recent years, the techniques of adsorptive cathodic stripping voltammetry (ACSV) and catalytic adsorptive stripping voltammetry (CASV) have undergone considerable progress [3–14]. The ACSV technique is based on adsorptive accumulation of the desired species (or its complex) on a hanging mercury drop electrode (HMDE) followed by electrochemical reduction of the adsorbed species. In CASV, the reduction current can be enhanced greatly if the reduction product of a voltammetric scan is chemically reoxidized in the presence of an oxidant on a time scale that is fast relative to the scan rate. The detection limit of CASV is very low, and it has excellent selectivity, sensitivity, accuracy and low cost of instrumentation. Thus it is very suitable for ultra-trace analysis.

In the last 20 years, several techniques of adsorptive cathodic stripping voltammetry and catalytic adsorptive stripping voltammetry have been developed for the determination of molybdenum [3–7,15–21]. All these methods are based on the adsorptive accumulation of a molybdenum complex. For example, molybdenum was determined using methyl thymol blue [3], Tiron [4], oxine [15,16], cupferron [17,18], mandelic acid [19], 3-methoxy-4-hydroxymandelic acid [20] and 2-(2′-thiazolylazo)-*p*-cresol [21]. The most sensitive catalytic adsorptive stripping voltammetric procedure was reported by Yokoi et al. [19] with a detection limit of 1.4 pM after 60 s accumulation.

Since the concentration of molybdenum in plants, water and soil is generally at parts per billion levels, therefore sufficient sensitivity method is required for the determination of molybdenum.

The new method described in this paper is based on the adsorptive accumulation of molybdenum (Mo)-pyrocatechol violet (PCV) complex and its catalytic effect on the electrochemical reduction of chlorate in an acidic medium. It is very sensitive and precise with large dynamic range for determination of low levels of molybdenum and is free from interference of common interfering ions such as iron.

The influence of variables on the peak current was studied by factorial design method. Factorial design is a powerful method for designing an experiment. The theory of full and fraction factorial design has been widely described elsewhere [22].

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2. Experimental

2.1. Reagents

All solutions were prepared with doubly distilled water. Chemicals used were of analytical grade and were purchased from E. Merck.

A solution of 1.0×10^{-3} M of PCV was prepared by dissolving 1.92×10^{-2} g of the reagent in water in a 50 ml volumetric flask. A solution of 2.0×10^{-5} M PCV was prepared by dilution of the stock solution with water.

A 1000 μg ml^{-1} solution of Mo(VI) was prepared by dissolving 0.2538 g of sodium molybdate dihydrate in water and diluting to 100 ml; more dilute solution were prepared by diluting this solution with water.

Potassium chlorate solution (0.5 M) was prepared by dissolving 15.318 g $KClO_3$ in water in a 250 ml volumetric flask.

Sulfuric acid solution was prepared by dissolving 5.5 ml of concentrated sulfuric acid (Merck, without Mo) in water and diluting to 100 ml.

2.2. Apparatus

Experiments were conducted by using a PAR (Princeton Applied Research) model 394 Polarographic analyzer equipped with a model 303A electrode system (EG&G). A conventional three electrode system, comprising a medium-sized hanging mercuric drop electrode, with a surface area of 1.8 mm^2, a platinum wire counter electrode and an Ag/AgCl (in saturated with KCl) reference electrode was used in all experiments. The reported potentials were referred to the Ag/AgCl electrode. Solutions were deoxygenated with high purity nitrogen for 4.0 min prior to each experiment and it was preformed under a nitrogen atmosphere.

2.3. Procedure

The sample solution (5.0 ml), containing 1.2 μM PCV, 0.4 M $KClO_3$ and 0.08 M H_2SO_4 was transferred into the voltammetric cell. The stirrer was switched on and the solution was purged with nitrogen gas for 4.0 min. The accumulation potential (0.1 V) was applied to a fresh HMDE for 30 s whilst stirring the solution. Following the accumulation period, the stirrer was stopped and after 5 s the voltammogram was recorded by applying a negative-going differential pulse scan from 0.1 to −0.1 V versus the Ag/AgCl reference electrode under the following instrumental conditions:

Pulse height, 20 mV; scan rate, 1 mV s^{-1}. The peak current for molybdenum was measured at about 15 mV and was recorded as a function of molybdenum concentration. A blank solution without molybdenum was used to obtain the blank peak current.

The experiment was designed by full factorial design [22]. We think that the effect of acid, PCV and chlorate concentrations and accumulation potential on the response (peak current) is two orders. Therefore, three levels for each factor were selected (Table 1), and 90 experiments ($3^4 + 9$ replicates) were run (factorial levels in replications: acid concentration, −1; chlorate concentration −1; PCV concentration and accumulation potential vary at −1, 0 and + 1 levels).

Table 1
Selected levels for each factor

Level	H_2SO_4 (M)	PCV (M)	$KClO_3$ (M)	Accumulation potential (*E*) (V)
−1	0.16	1×10^{-7}	0.1	−0.2
0	0.08	2×10^{-7}	0.3	0.0
+1	0.04	2×10^{-6}	0.4	0.2

Data were processed with a specially written MATLAB program (the math works Inc., version 7.0). The optimum values of parameters were calculated with MATLAB programming.

3. Results and discussion

3.1. Preliminary investigations

Molybdenum can be form a complex with the PCV. The PCV or pyrocatechol sulfonaphthalein is a dye in the triphenylmethane series, and it is a sensitive reagent for the molybdenum.

Fig. 1 shows differential pulse voltammograms for Mo(VI)-PCV and Mo(VI)-PCV-ClO_3^- in 0.08 M H_2SO_4. As can be seen in Fig. 1b, in the absence of chlorate the reduction current is rather small. Addition of 0.4 M potassium chlorate causes an increase of the molybdenum reduction current in comparison to the Mo(VI)-PCV complex (Fig. 1c), this suggesting a catalytic process.

In cyclic voltammogram, when scanning the electrode potential for the Mo(VI)-PCV-ClO_3^- in the negative direction, a cathodic peak at −110 mV vs. Ag/AgCl reference electrode was observed. In addition, the reverse scan gave another cathodic peak at −86 mV vs. Ag/AgCl electrode (Fig. 2a) on the other hand, in the absence of chlorate and in the reverse potential scan, no cathodic wave was observed (Fig. 2b), suggesting a catalytic process. Also analysis of a Mo(VI)-PCV system in presence of high amounts of chlorate (relative to molybdenum) at various scan rates shows a linear relationship between $I_p/\upsilon^{1/2}$ and υ^{-1}

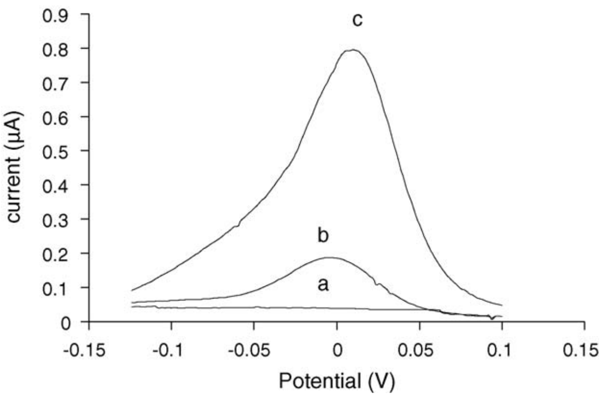

Fig. 1. Differential pulse voltammograms for Mo(VI)-PCV and Mo(VI)-PCV-ClO_3^- in, 0.4 M chlorate and 30 s accumulation at 0.1 V. (a): 0.08 M H_2SO_4, 1.2×10^{-6} M PCV (b) a plus 10 ng ml^{-1} Mo(VI), (c) a plus 5.0 ng ml^{-1} Mo(VI) and 0.4 M chlorate.

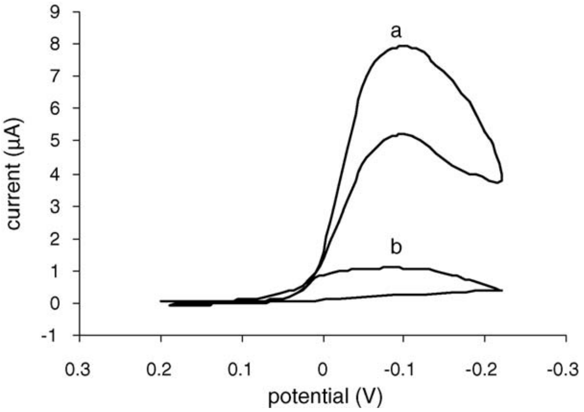

Fig. 2. Cyclic voltammograms of 10.0 ng ml^{-1} Mo(VI) in the 0.08 M H_2SO_4 containing 1.2×10^{-6} M PCV (a) with 0.4 M chlorate (b) without chlorate. Accumulation potential 0.1 V, accumulation time 30 s and scan rate 50 mV s^{-1}.

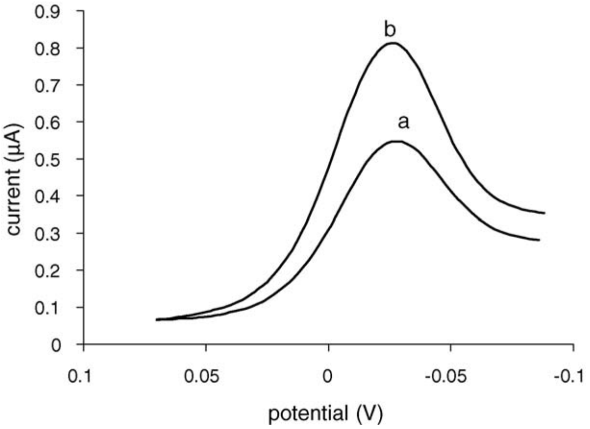

Fig. 3. Differential pulse voltammograms of Mo(VI)-PCV-ClO_3^-, recorded without an accumulation period (curve a), and after 30 s accumulation at 0.1 V (curve b).

(I_p is cathodic current (nA) and υ = scan rate (mV s^{-1})) with a regression coefficient of 0.9957 (and slope of 1668) involving mechanism of EC′. On the basis of the above results, the catalytic mechanism of ClO_3^- in the medium containing Mo(VI) and PCV is a typical electrochemical–chemical process.

On the other hand an E_p–log(scan rate) analysis of a series of linear scan voltammograms of (Mo(VI)-PCV-ClO_3^-) gave a slope of 120 mV indicating a one-electron transfer reduction process [23].

The catalytic effect of molybdenum on the reduction of chlorate is well-known. A possible reaction mechanism is that Mo(V) (which is generated at the electrode surface upon the reduction of pyrocatechol violet complex of Mo(VI)) reduces chlorate [Cl(V)] to a meta-stable reduction product [Cl(IV)] [19] whilst the thus generated Mo(VI) is re-reduced at the electrode to Mo(V). Thus contributing repeatedly to the reduction current. To confirm of this mechanism, square wave (SW) studies were made. In these studies, it can be seen that the heights of the split SW peaks are sensitive to the concentration of the catalytic agent. In the presence of chlorate, forward SW component gradually increases, whereas backward SW component diminishes, therefore the splitting vanishes under high rate of the catalytic reaction, which it can be applied for qualitative characterization of surface catalytic electrode reaction [7]. Also the net SW peak of Mo-PCV system in the presence of chlorate shifts in the negative potentials by increasing of rate of catalytic regeneration. This matter implies that the catalytic effect of chlorate is a simple redox reaction with Mo(V) to yield back the Mo(VI) complex [7].

Fig. 3 Show differential pulse voltammograms of Mo(VI)-PCV-ClO_3^-, recorded without an accumulation period (curve a), and after 30 s accumulation at 0.1 V (curve b). This increase in response shows that Mo(VI)-PCV has adsorptive characteristics at the mercury electrode.

3.2. *Factorial design and optimization*

In this experiment, the effects of chemical parameters such as acid, Pyrocatechol violet and chlorate concentrations and instrumental parameters such as accumulation potential and the interaction of these parameters on peak current by full factorial design were studied.

A preliminary study shows that with increasing accumulation time and decreasing of scan rate, peak current (ΔI_p) slightly increases; therefore, we consider constant amount of 30 s and 1 mV s^{-1} as the accumulation time and scan rate for simplicity.

In making the model, the response (the peak current) was written as a function of acid, PCV, chlorate concentrations and accumulation potential and all possible interactions. The coefficients of these parameters were obtained by multiple least-squares regression. For each parameter and interaction, the parameter coefficient, the standard error (S.E.), the t value for the null hypothesis (H_0), and the corresponding P value were calculated. A program written in MATLAB was used to perform the calculations. The null hypothesis states that the value of the parameter coefficient is zero. The P value is the probability that a parameter coefficient can be zero. If the P value for each parameter is greater than 0.05, the parameter has no significant effect in the model (confidence limit, 95%), and can be eliminated (the value of the parameter coefficient is taken to be zero). But the model was kept hierarchical; i.e., a factor with a P value greater than 0.05, but with the higher order of this factor having a P value less than 0.05, was not removed. Finally nonzero coefficients and their related t and P values were calculated (Table 2).

The analysis of variance (ANOVA) of the model is shown in Table 3. The F value of the model (regression) describes that the regression at the confidence limit of 99.9% (p = 0.0001) is significant, and the model has a correlation coefficient 0.9899. The root mean square error (RMSE) is 39.53, which corresponds to a relative error of 6.5% in the measured peak currents. There is no lack of fit in the confidence limit 95% (calculated $F_{\text{lack of fit}}$ is less than the critical value). In Fig. 4 residuals are plotted versus number of experiments, which predicts that we have hemoscedastic error in our experiment.

From the model, a program in MATLAB was written to calculate the optimum value for the each parameter. Within the confidence limit of 95%, the model shows three significant

Table 2

Parameter	Parameter value	S.E.	t for H_0	P value
Intercept	178.8	72.90	2.45	0.0069
Acid	−2405.3	298.67	−8.05	0.0001
ClO_3^-	201.2	56.04	3.59	0.0001
PCV	11448.0	497.99	22.98	0.0001
E	−94.3	44.18	−2.13	0.0166
$(Acid)^2$	1986.8	286.13	6.92	0.0001
$(ClO_3^-)^2$	−33.4	11.13	−3.00	0.0013
$(PCV)^2$	−24788.8	9060.00	−27.36	0.0001
E^2	413.1	130.95	3.15	0.0008
Acid × ClO_3^-	7898.2	550.30	14.35	0.0001
Acid × PCV	72.3	46.99	1.53	0.0630
PCV × E	−622.3	93.14	−6.68	0.0001
$ClO_3^- \times (Acid)^2$	−5838.9	536.45	−10.88	0.0001
PCV × $(Acid)^2$	30.3	19.35	1.56	0.0594
$E \times (ClO_3^-)^2$	−14.9	9.65	−1.54	0.0618

Table 3
The analysis of variance (ANOVA) of the model

Source	d.f.	Sum of squares	F value	P value
Total	89	6.9505×10^6		
Treatment (regression)	14	6.8114×10^6	262.2930	0.0001
Residual	75	1.3911×10^5		
Lack of fit	66	1.3149×10^5	2.3515	
Pure error	9	7.6254×10^3		
R^2	0.9800			
RMSE	39.53			
Mean	607.5331			
C.V.	6.5077			

second-order interactions, three significant third-order interactions, and four significant quadratic effects. As shown is Table 2, PCV concentration has a significant effect on the response. The later significant effect is the acid concentration. Although chlorate concentration in studied range (0.1–0.4 M) has lower effect but it's effect is very strong relative to without chlorate solution (Fig. 2). The effect of accumulation potential is smaller than acid, PCV and chlorate concentrations. In quadratic effects, the effect of PCV is significant because this parameter has important effect on the reaction, and the negative sign of coefficient describe that the peak current has the maximum value with respect this parameter. In the second-order interaction, the interaction of acid concentration with chlorate concentration (Fig. 5) is very important, as in low chlorate concentration variation of current with respect to different acid concentrations, is low, but in higher chlorate concentration these variations are high. Between the other second order interactions, the interaction of PCV with accumulation potential and PCV with acid concentration are in the second and third position, respectively. Between third-order interactions, the interaction of second power of acid concentration with chlorate concentration is important.

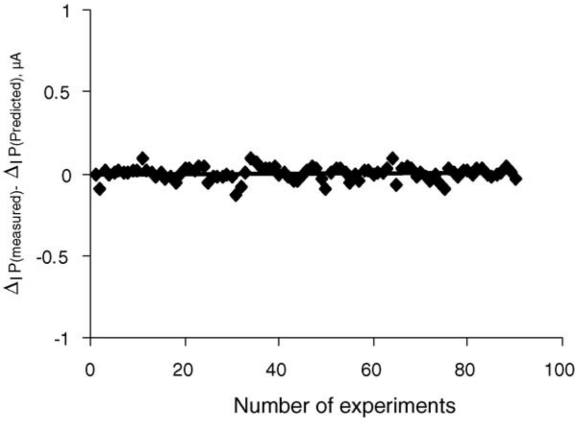

Fig. 4. Residuals vs. number of experiments.

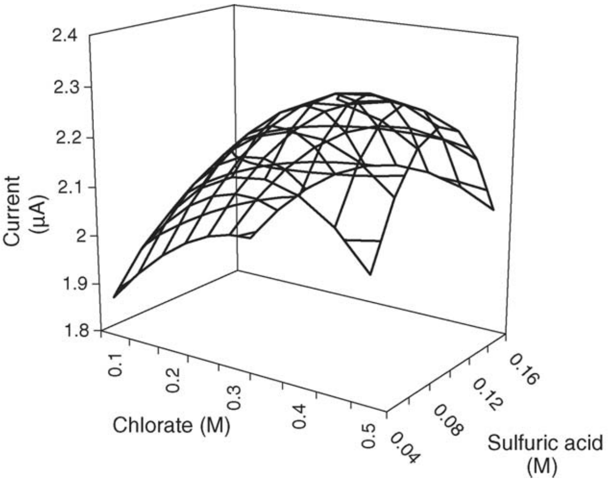

Fig. 5. The interaction of acid concentration with chlorate concentration.

In Fig. 6, the current calculated from the model is plotted versus the measured current. The correlation coefficient for the plot is 0.9899, which indicates good performance for the model.

The optimum values for acid, PCV, chlorate concentrations and accumulation potential calculated with MATLAB programming are 0.08 M, 1.2×10^{-6} M, 0.4 M and 0.1 V, respectively.

3.3. Figures of merit

3.3.1. Calibration curve, detection limit and reproducibility of the method

Under the optimum conditions achieved by factorial design analysis, two regions for calibration were obtained. The first calibration curve was obtained in the range of

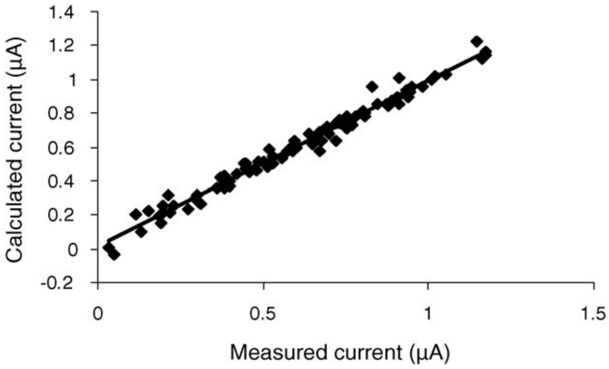

Fig. 6. The current calculated from the model vs. the measured current.

Table 4
Maximum tolerable concentration of interfering species optimum reagent-concentration and 30 s accumulation at 100 mV, Mo(VI) concentration 5.0 ng ml^{-1}

Species	Tolerance limit (w/w)
Hg^{2+}, K^+, Fe^{3+}, Fe^{2+}, Ba^{2+}, Na^+, Cl^-, $Cr_2O_4{}^{2-}$, $NH_4{}^+$, $CO_3{}^{2-}$, Rh(III), Pd(II), Mg^{2+}, Ca^{2+}, Zn^{2+}, $SO_3{}^{2-}$, Pb(II), $NO_3{}^-$, As(III), Ce(IV), $BiO_3{}^-$, $C_2O_4{}^{2-}$, Mn^{2+}, U(VI), V(V), Cu^{2+}, Os(VIII), CN^-, Si(IV), $S_2O_3{}^{2-}$, $SO_4{}^{2-}$	1000[a]
Sn^{2+}	100
$IO_3{}^-$	50
Ru(III)	20
W(VI)	1

[a] Maximum concentration tested.

1.0×10^{-3}–20.0 ng ml^{-1} and the second in the range of 20.0–100.0 ng ml^{-1}. The equations of the calibration curves in two regions are:

$$\Delta I_{\mathrm{p}} = 35.98 + 220.80(\mathrm{Mo(VI)})_{(\mathrm{ng\,ml^{-1}})}$$

$$(R^2 = 0.9940, \quad n = 17)$$

and

$$\Delta I_{\mathrm{p}} = 26.89 + 35.05(\mathrm{Mo(VI)})_{(\mathrm{ng\,ml^{-1}})}$$

$$(R^2 = 0.9904, \quad n = 7)$$

A detection limit ($C_{\mathrm{LOD}} = 3\,S_{\mathrm{b}}/m$, where S_{b} is the standard deviation for five replicates determination of the blank signal and m is the slope of the calibration curve) of 0.2 pg ml^{-1} for Mo(VI) was obtained. The relative standard deviation for five replicates measurement of 0.1, 1 and 10 ng ml^{-1} are 1.4, 1.4 and 1.2%, respectively.

3.3.2. Interference study

The effects of more than 35 ions on the determination of 5.0 ng ml^{-1} of Mo(VI) were studied with the optimized conditions described above. The tolerance limit is defined as the foreign-ion concentration causing an error smaller than 3.0% for the determining 5.0 ng ml^{-1} molybdenum. The results are presented in Table 4. The results indicate that many of ions did not interfere. Only W(VI) interfered at level similar to that molybdenum. The fact that iron, copper, lead and zinc did not interfere is of particular significance considering their major interference in most the previously reported systems.

Comparative analytical figures of merit for different sensitive CASV techniques for the determination of molybdenum have been given in other works [3,4]. By using their results, it can be shown that under conditions at which no purification has been performed on the blank, the selectivity of the proposed method is comparable to those of the previously reported methods, while a very better linear dynamic range and sensitivity can also be obtained.

Table 5
Determination of molybdenum in Damavand mineral water and some analytical grade acids

Sample	Mo added (ng ml^{-1})	Total Mo found (ng ml^{-1})	Recovery of spike (%)
Mineral water	–	1.25	–
Mineral water	2.00	3.41	108.0
Mineral water	3.00	3.99	91.3
H_2SO_4	–	0.16	–
H_2SO_4	0.10	0.26	100.0
H_2SO_4	0.20	0.34	90.0
H_2SO_4	0.30	0.49	110.0
HNO_3	–	0.14	–
HNO_3	0.20	0.32	90.0
HNO_3	0.30	0.43	96.7

3.3.3. Real sample analysis

The proposed method was successfully applied to the determination of molybdenum in a mineral water sample and some analytical grade acids (Table 5). For water analysis, the sample was filtered using filter paper, and then was used for determination of molybdenum content by standard addition method. The acid samples were neutralized and then 0.15 M sulfuric acid and 0.19 M nitric acid (neutralized samples) analyzed by standard addition method. The data obtained for samples spiked with molybdenum showed good recoveries.

4. Conclusions

The present study demonstrates that catalytic stripping voltammetric determination of molybdenum in presence of PCV and chlorate is excellent for determination of ng ml^{-1} concentrations in real samples, of molybdenum because of high sensitivity, very large dynamic range, simplicity and speed, a combination very better from previously reported systems.

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