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Flow-injection catalytic spectrophotometic determination of molybdenum(VI) in plants using bromate oxidative coupling of *p*-hydrazinobensenesulfonic acid with *N*-(1-naphthyl)ethylenediamine

Shigenori Nakano*, Chie Kamaguchi, Naoki Hirakawa

Department of Regional Environment, Faculty of Regional Sciences, Tottori University, Koyama-cho, Tottori 680-8551, Japan

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ABSTRACT

A novel flow-injection spectrophotometry has been developed for the determination of molybdenum(VI) at nanograms per milliliter levels. The method is based on the catalytic effect of molybdenum(VI) on the bromate oxidative coupling of *p*-hydrazinobenzenesulfonic acid with *N*-(1-naphthyl)ethylenediamine to form an azo dye (λ_{max} = 530 nm). Chromotropic acid (4,5-dihydroxy-2,7-naphthalenedisulfonic acid) acted as an effective activator for the molybdenum(VI)-catalyzed reaction and increased the sensitivity of the method. The reaction was monitored by measuring the change in absorbance of the dye produced. The proposed method allowed the determination of molybdenum(VI) in the range 1.0–20 ng mL^{-1} with sample throughput of 15 h^{-1}. The limit of detection was 0.5 ng mL^{-1} and a relative standard deviation for 10 ng mL^{-1} molybdenum(VI) (n = 10) was 2.5%. The interfering ions were eliminated by using the combination of a masking agent and on-line minicolumn packed with cation exchanger. The present method was successfully applied to the determination of molybdenum(VI) in plant foodstuffs.

1. Introduction

Determination of molybdenum is important, because it plays a significant role in a wide variety of plants and animals [1,2]. This element is essential for bacteria in the fixation of atmospheric nitrogen and in the reduction of nitrate to nitrite. Its deficiency or excess can cause damage to organisms. Molybdenum and its compounds have been widely used in many industrial processes such as metal alloys, pigments, lubricants and catalysts; industrial effluents containing excess of molybdenum can affect biological systems. Thus rapid, selective and sensitive methods for the molybdenum determination are still required in order to clarify its behavior in the organism and/or environment.

A number of spectrophotometric methods based on complex formation are used for the determination of molybdenum [3–5]. Owing to their low sensitivity and selectivity, preconcentration and/or separation steps are usually necessary. There have been reported highly sensitive analytical techniques for the molybdenum determination such as spectrofluorimetry [6], voltammetry [7], atomic absorption spectrometry (AAS) [8,9], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [10], and ICP-mass spectrometry (ICP-MS) [11]. ICP techniques necessitate the use of rather high cost instruments.

Kinetic-based methods for the determination of trace amounts of elements have been reported in last three decades [12–15]. The advantages of these methods are extremely high sensitivity with simple procedures and inexpensive apparatus. Table 1 shows kinetic-catalytic methods for the determination of molybdenum using spectrophotometry [16–29]. In these methods, hydrogen peroxide oxidation of iodide [16–19], 2,4-diaminophenol [20], chlorpromazine [21], L-ascorbic acid [22–24], pyrogallol red [25], 2-aminophenol [26] and 1-amino-2-naphthol-4-sulfonic acid [27] were used as indicator reactions. The reactions of toluidine blue with stannous chloride [28] and metanil yellow with hydrazine [29] were also utilized as indicator reactions. These methods are capable of determining molybdenum at ng mL^{-1} and/or sub-ng mL^{-1} levels. Among them, the catalytic method based on the oxidation of L-ascorbic acid by hydrogen peroxide had the highest sensitivity (Table 1); however, its drawback was low stability of L-ascorbic acid solution [30].

The oxidative coupling of *p*-hydrazinobenzenesulfonic acid (HBS) with 1-naphthylamine or *m*-phenylenediamine in the presence of chlorate has been utilized as an indicator reaction for the catalytic determinations of vanadium(V) [31] and selenium(IV) [32,33]. The reaction of HBS with *N*-(1-naphthyl)ethylenediamine (NED) have also used as an indicator reaction for the catalytic determination of selenium(IV, VI) [34]. We found that molybdenum(VI)

* Corresponding author. Fax: +81 857 31 5109.
E-mail address: nakano@rstu.jp (S. Nakano).

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Table 1
Catalytic-spectrophotometric methods for the determination of molybdenum.

Indicator reaction	Procedure	Dynamic range (ng mL^{-1})	Masking agent or separation	Application	Reference
Iodide + H_2O_2	FIA	1–40	Cation exchanger	Plants	[16]
+ CPC	Reaction rate	2–150	–	Soil extracts	[17]
	MCFA	1–50	Extraction	Plants	[18]
	Reaction rate	1–50	Cation exchanger	Wine	[19]
2,4-Diaminophenol + H_2O_2	Reaction rate	48–480	Anion exchanger	Steel	[20]
Chlorpromazine + H_2O_2	Initial rate	3–60	–	Hot spring water	[21]
Ascorbic acid + H_2O_2 + PDA	Fixed time	0.06–3	CDTA	River, rain and tap water	[22]
	FIA	0.06–3	CDTA	River, lake, rain and tap water	[23]
	ASCFA	0.006–0.96	Cation exchanger	Lake and sea water	[24]
Pyrogallol red + H_2O_2	Reaction rate	10–500	Cation exchanger	Plant and steel	[25]
2-Aminophenol + H_2O_2	Fixed time	0.1–11	Coagulation	River, well and waste water	[26]
ANS + H_2O_2	Fixed time	0.027–2.5	DTPA	Waste, rain, tap, bottled and polluted water	[27]
HBS + NED + bromate	FIA	1–20	Cation exchanger	Plants	This work
Toluidine blue + $SnCl_2$	Reaction rate	48–465	Extraction	–	[28]
Metanil yellow + hydrazine	Fixed time	20–160	Extraction	Bean	[29]

CPC = hexadecylpyridinium chloride (cetylpyridinium chloride), PDA = *o*-phenylenediamine, ANS = 1-amino-2-naphthol-4-sulfonic acid, HBS = *p*-hydrazinobenzenesulfonic acid, NED = *N*-(1-naphthyl)ethylenediamine, FIA = flow-injection analysis, MCFA = mono-segmented continuous-flow analysis, ASCFA = air-segmented continuous-flow analysis, CDTA = trance-1,2-cyclohexanediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid, DTPA = diethylenetriaminepentaacetic acid.

catalytically accelerates the oxidative coupling of HBS with NED in the presence of bromate. In this molybdenum(IV)-catalyzed reaction, chromotropic acid (4,5-dihydroxy-2,7-naphthalenedisulfonic acid, CTA) acted as an effective activator. This catalyzed reaction was adopted to flow-injection analysis for molybdenum(IV). Although the reaction has an induction period which needs a long reaction time to obtain higher sensitivity, this disadvantage was overcome by setting up the time-lag between addition of reagents. This paper describes a sensitive flow-injection method for the determination of molybdenum(VI) based on its catalytic effect on this oxidative coupling. The proposed method allows the determination of molybdenum(VI) in the range 1.0–20 ng mL^{-1}. Interference from iron(III) was eliminated by using the combination of *N*,*N*,*N*′,*N*′-ethylenediaminetetrakis(methylenephosphonic) acid (EDTPO) as a masking reagent and on-line cation-exchange column. The method has been applied to the determination of molybdenum(VI) in plant foodstuffs.

2. Experimental

2.1. Reagents

Chemicals were of analytical reagent grade and used without further purification unless stated otherwise. Water used for the preparation of solutions was purified by a Millipore Milli-Q water-purification system.

A commercially available molybdenum(VI) solution (1.0 mg mL^{-1}) for atomic absorption spectrometry (Kanto Kagaku, Japan) was used as a standard solution. The working solutions were prepared fresh daily by appropriate dilution of the standard solution with 1.0×10^{-2} mol L^{-1} hydrochloric acid.

A HBS (8.0×10^{-3} mol L^{-1}) solution including CTA (1.0×10^{-2} mol L^{-1}), EDTPO (8.0×10^{-4} mol L^{-1}) and Tween 80 (0.02% (w/v)) was prepared as follows: 0.395 of *p*-hydrazinobenzenesulfonic acid, hemihydrate (Tokyo Kasei Co., Japan) and 1.00 g of chromotropic acid, disodium salt, dihydrate (Dojindo Lab., Japan) were dissolved in water and then 4.0 mL of 5.0×10^{-2} mol L^{-1} EDTPO and 10 mL of 0.5% (w/v) Tween 80 was added. Finally the pH of the solution was adjusted to *ca.* 1.8 by adding 1.0 mol L^{-1} hydrochloric acid and the solution was diluted to 250 mL with water.

A 7.0×10^{-4} mol L^{-1} NED solution was prepared by dissolving 0.045 g of *N*-(1-naphthyl)ethylenediamine dihydrochloride (Wako Pure Chemical Co., Japan) in 250 mL of water. A 0.80 mol L^{-1} sodium bromate solution was also prepared by dissolving the compound in water.

2.2. Apparatus

A diagram of the flow system for the determination of molybdenum(VI) is schematically shown in Fig. 1. The system consisted of two double plunger micro-pumps (Sanuki Kogyo, DM2M-10264), a six-way valve (Sanuki Kogyo, SVM-6M2) with a sample loop, a cation-exchange column, a thermostated bath (Toyo Kagaku LH-1000C), a spectrophotometer (Soma Kogaku S-3250) equipped with 8-μL flow cell (optical path length, 10 mm) and a recorder (Chino Model EB 22005). The flow lines were made from Teflon tubing (0.5 mm i.d.) and connectors. A Toa HM-5S pH meter was used for pH measurements. A Hitachi Model U-2000A spectrophotometer was used for the measurement of absorption spectra and absorbance. ICP-AES (Rigaku Ciros CCD) was used for the comparative determination of molybdenum.

The cation-exchange column was used to remove foreign ions such as iron(III) [16]. The column was prepared as follows: Dowex 50WX8 (100–200 mesh, proton form; Dow Chemical Co.) was slurry-packed in a Teflon tubing (1 mm i.d., 50 mm length). Quartz wool was used to prevent leakage of the packing resin from the column. Before experiments, the column was successively washed with 20 mL of 4 mol L^{-1} hydrochloric acid and 50 mL of water, and then it was conditioned in the present flow system for about 10 min by propelling the carrier solution. When the reproducibility of the same sample became poorer, which accepted as more than capac-

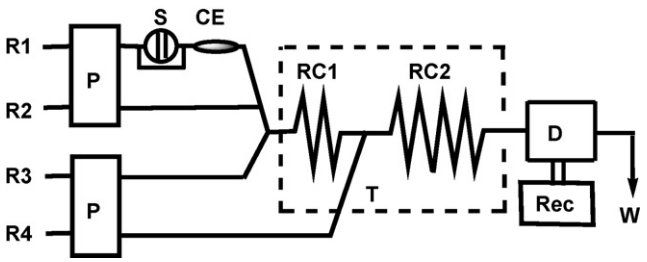

Fig. 1. Flow system for the determination of molybdenum(VI). R1–R4, reservoir; P, pump; S, sample injector; CE, cation exchange column; RC1 and RC2, reaction coils; T, thermostated bath; D, detector; Rec, recorder; W, waste. Conditions as in Table 2.

ity of the column, 200 μL of 4 mol L^{-1} hydrochloric acid and 400 μL of water in sequence were injected by the six-way valve to elute these ions.

2.3. Sample preparation

Plant foodstuffs purchased from the market were ground (*ca.* 100 mesh) and dried at 105 °C for 2 h. An accurately weighted sample was transferred into a porcelain crucible and was ashed at 600 °C for 4 h. After cooling to room temperature, the resulting ash was moistened with 1 mL of water and mixed with 10 mL of 6 mol L^{-1} nitric acid. The mixture was evaporated near to dryness on a hot plate at about 150 °C. The residue was dissolved with 10 mL of 0.10 mol L^{-1} hydrochloric acid. The solution was filtered by using filter paper (Advantec No. 5C). This procedure was repeated with 0.1 mol L^{-1} hydrochloric acid until the total volume of filtrate was 40 mL. The resulting solution was transferred to a 50 mL volumetric flask finally and made up to volume with the acid.

2.4. Procedure

The selected conditions for the molybdenum(VI) determination are given in Table 2. In the flow system as shown in Fig. 1, a carrier solution (1.0×10^{-2} mol L^{-1} hydrochloric acid) in reservoir R1, a HBS solution including CTA, EDTPO and Tween 80 in R2, bromate and NED solutions in R3 and R4, respectively, were propelled at a flow rate of 0.5 mL min^{-1} each. A 200 μL aliquot of sample solution was introduced into the carrier stream and was merged with the HBS solution. The mixed solution was sent to the first reaction coil (RC1, 5 m) immersed in a thermostated bath at 60 °C. Then, the solution was mixed again with NED streams and sent to the second reaction coil (RC2, 16 m) immersed in the thermostated bath. The colored solution was passed to the flow-through cell where the absorbance of the dye produced at 530 nm was measured and continuously recorded.

3. Results and discussion

In the acidic solution, HBS ($HO_3S(C_6H_4)NHNH_3^+$) is oxidized by bromate to *p*-sulfobenzendiazonium ion ($HO_3S(C_6H_4)N^+{\equiv}N$) which is then coupled with NED to form a red azo dye.

$$HO_3S(C_6H_4)NHNH_3^+ + BrO_3^- + 2H^+ \rightarrow HO_3S(C_6H_4)N^+{\equiv}N + Br^- + 3H_2O \quad (1)$$

$$HO_3S(C_6H_4)N^+{\equiv}N + NED \rightarrow \text{Azo dye} \quad (2)$$

Although this oxidative coupling is slow process, it proceeds rapidly in the presence of molybdenum(VI) which acts as a catalyst in Eq. (1). CTA as an activator increases the rate of the molybdenum(VI)-catalyzed reaction.

Fig. 2 shows the absorption spectra of reaction products in the absence and presence of molybdenum(VI). Both have an absorption maximum at 530 nm. The absorbance changes were thus monitored at this wavelength.

3.1. Formation curves of the dye

Formation curves of the dye were prepared by a batch procedure in order to presume the reaction mechanism. Fig. 3a shows the formation curves of the dye in the presence and absence of molybdenum(VI), which were obtained by the addition of HBS, NED and bromate solutions in this order. As can be seen, an induction period was observed. This may be explained as follows. In excess

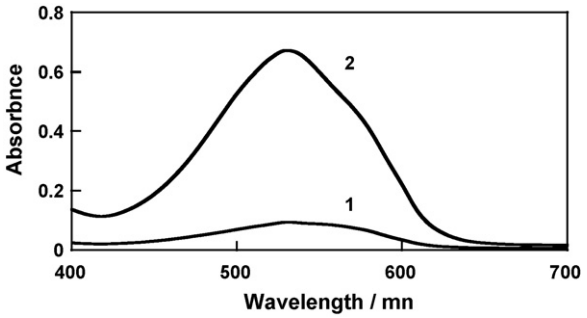

Fig. 2. Absorption spectra of reaction products. 1, Reagent blank; 2, 2.0 ng mL^{-1} molybdenum(VI). C_{HBS}, 6.0×10^{-4} mol L^{-1}; C_{NED}, 4.0×10^{-4} mol L^{-1}; C_{NaBrO_3}, 2.4×10^{-2} mol L^{-1}; C_{CTA}, 2.0×10^{-3} mol L^{-1}; $C_{Glycine}$, 1.0×10^{-2} mol L^{-1}; Reaction pH, 2.4; Temperature, 45 °C. Reaction time, 50 min.

concentrations of bromate, bromide formed in Eq. (1) is oxidized to bromine [35], which reacts with HBS.

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O \quad (3)$$

$$HO_3S(C_6H_4)NHNH_3^+ + Br_2 \rightarrow HO_3S(C_6H_4)N^+{\equiv}N + 2Br^- + 4H^+ \quad (4)$$

In this reaction system, bromine was slowly yielded as a reaction product of HBS with bromate and was observed at 390 nm (data are not shown). In order to shorten the induction period, the order of addition of reagent solutions was changed and an incubation time was set up, i.e., the HBS and bromate solutions were firstly mixed in the reaction vessel and incubated for a given time, and then NED solution was added to the reaction vessel. Fig. 3b shows the formation curves obtained at the incubation time of 20 min; induction period was not observed. The time lag between the addition of reagents was made it possible to realize the higher sensitivity. Therefore, the flow system having oxidation and coupling reaction coils (RC1 and RC2) was constructed as shown in Fig. 1.

3.2. Selection of activator

The rate of metal-catalyzed reaction can be accelerated by the presence of a suitable ligand as an activator [12–15]. It can form a catalytically active complex with metal ion and vary the redox

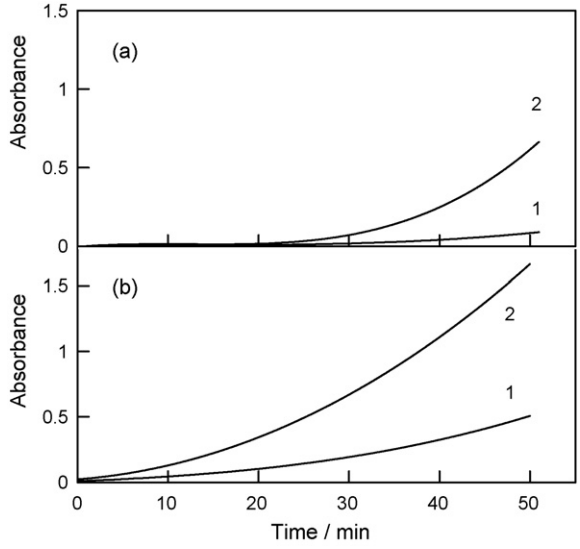

Fig. 3. Formation curves for azo dye. Incubation time in minutes: (a) 0; (b) 20. 1, Reagent blank; 2, 2.0 ng mL^{-1} molybdenum(VI). Conditions as in Fig. 2.

Table 2
Selected conditions for the determination of molybdenum(VI).

Reservoir	R1	1.0×10^{-2} mol L^{-1} HCl (carrier)
	R2	8.0×10^{-3} mol L^{-1} HBS/1.0×10^{-2} mol L^{-1} CTA/8.0×10^{-4} mol L^{-1} EDTPO/2.0×10^{-2}% (w/v) Tween 80
	R3	0.80 mol L^{-1} $NaBrO_3$
	R4	7.0×10^{-4} mol L^{-1} NED
Individual flow rate		0.50 mL min^{-1}
Sample volume		200 μL
Column		Dowex 50WX8 (1 mm i.d., 50 mm length)
Reaction temperature		60 °C
Oxidation coil length		5 m
Coupling reaction coil length		16 m
Reaction pH		2.2
Detector		Spectrophotometer (530 nm)

potential of the metal ion pair ($M^{(n+1)+}/M^{n+}$) system. Multidentate ligands capable of complexing the catalyst and forming hydrogen bonds with oxidant also facilitate the formation of the charge-transfer complex [36]. Thus, it yields better sensitivity and lower limit of detection.

Some ligands such as CTA, L-cysteine, gallic acid, 2,6-pyridinedicarboxylic acid, sulfite and thiourea were examined as potential activators for molymdenum(VI) by using the flow system without column. Among them, CTA was exhibited the strongest activating effect on the catalysis of molymdenum(VI). Fig. 4 shows the effect of CTA concentration on the peak height due to catalyzed reaction and height of baseline due to uncatalyzed reaction. These heights increased with increasing the CTA concentration. For the procedure, 1.0×10^{-2} mol L^{-1} of CTA solution was selected to ensure high sensitivity and reproducibility.

3.3. Effect of flow-injection variables

In the presence of CTA, variables affecting the sensitivity were optimized by using the flow system without column. Slower flow rate provided higher both the heights of peak and baseline because of longer reaction time. The flow rate in the present flow-injection system was fixed at 0.5 mL min^{-1}. The effect of reaction temperature on the peak height was examined in the range 45–70 °C. Higher sensitivity was obtained at higher temperature, but the height of baseline also increased with increasing temperature, which led to poorer reproducibility. The reaction was carried out at 60 °C by considering the sensitivity and reproducibility.

The effect of reaction coil lengths of RC1 and RC2 was also examined. Longer length of both coils increased both the heights of peak and baseline because of longer reaction time. The reaction coil lengths of RC1 and RC2 were selected as 5 m and 16 m, respectively, for the sake of sensitivity and sample throughput. An increase in the sample size up to 200 μL increased the peak height. In 200 μL or more sample sizes, the peak height increased gradually; the sample size was fixed at 200 μL for the procedure.

3.4. Effect of chemical variables

The effect of reaction pH was examined in the range 1.5–3.5. A decrease in pH value increased the heights of peak and baseline. By considering the baseline stability, the reaction was carried out at pH 2.2.

Fig. 5 shows the effect of HBS concentration on the catalyzed and uncatalyzed reactions. As can be seen, peak height increased with increasing HBS concentration up to 8.0×10^{-3} mol L^{-1}; this HBS concentration was thus used for the procedure. Tween 80 was added to the HBS solution in order to prevent the adsorption on the reaction coil of the azo dye produced and to reduce peak tailing, which led to high sampling frequency. For the procedure, 2.0×10^{-2}% (w/v) Tween 80 was adopted because it did not affect the peak height at above the concentrations of 1.0×10^{-2}% (w/v).

An increase in bromate concentration increased the heights of peak and baseline as shown in Fig. 6. By balancing the heights of peak and baseline, the bromate concentration was selected at 0.80 mol L^{-1}. Higher NED concentrations gave higher heights of peak and baseline. A 7.0×10^{-4} mol L^{-1} NED concentration was chosen for the sake of the baseline stability.

3.5. Elimination of iron

It was observed that iron(III) seriously interfered with the molybdenum determination due to its catalytic effect. To suppress the interference from iron(III), complexing agents for iron(III)

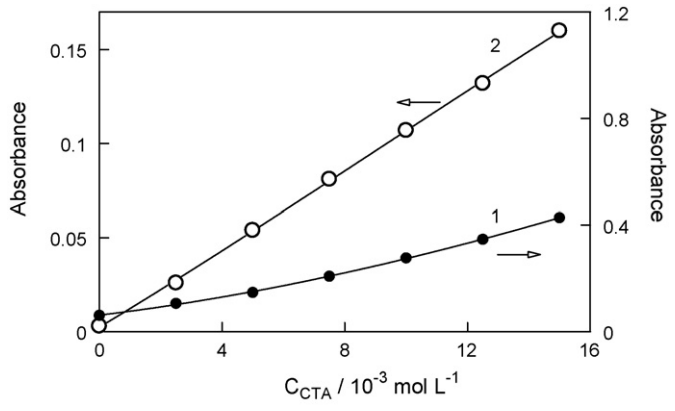

Fig. 4. Effect of CTA concentration on the catalyzed and uncatalyzed reactions. 1, Baseline; 2, 10 ng mL^{-1} molybdenum(VI). Conditions as in Table 2 except for CTA concentration.

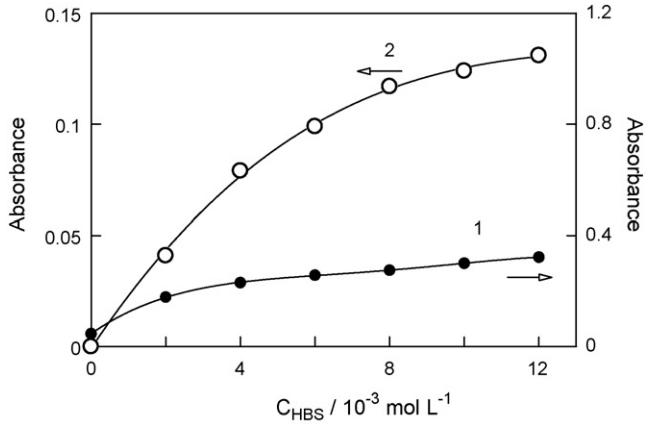

Fig. 5. Effect of HBS concentration on the catalyzed and uncatalyzed reactions. 1, Baseline; 2, 10 ng mL^{-1} molybdenum(VI). Conditions as in Table 2 except for HBS concentration.

Table 3
Tolerance limits for foreign ions in the determination of 5.0 ng mL^{-1} Mo(VI).

Tolerance limit (ng mL^{-1})	Ion added
10000[a]	As(V), Ce(III), K(I), Mg(II), Na(I), NH_4(I), Ni(II), Pb(II), BO_3^{3-}, ClO_4^-, NO_3^-, SO_4^{2-}
5000	Ca(II), Co(II), Hg(II)
1000	Al(III), Ba(II), Cu(II), Fe(II), Mn(II), Zn(II), Br^-
500	Cd(II), Cr(III), Fe(III), Sr(II), F^-, PO_4^{3-}, SCN^-
100	Ag(I), As(III), Te(IV), Ti(IV), Citrate, Oxalate, Tartrate
50	Bi(III), Ce(IV), I^-, NO_2^-, W(VI)[b]
20	V(V), V(IV)
10	Cr(VI), Se(IV), Sn(II), Sn(IV)
5	W(VI)

[a] Maximum concentration examined.
[b] Add 500 ng mL^{-1} Sr(II).

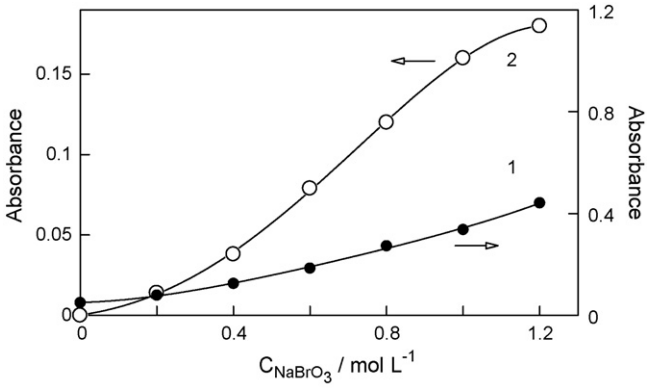

Fig. 6. Effect of bromate concentration on the catalyzed and uncatalyzed reactions. 1, Baseline; 2, 10 ng mL^{-1} molybdenum(VI). Conditions as in Table 2 except for bromate concentration.

such as EDTA, EDTPO and *trans*-1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetraacetic acid were examined as masking agents by adding them to reservoir R2; these agents masked iron(III). Since EDTPO scarcely affected the catalyzed reaction, it was chosen as a masking agent and suppressed the interference up to 20-fold excess of iron(III) at the concentrations above 4.0×10^{-4} mol L^{-1}. EDTPO concentration was fixed at 8.0×10^{-4} mol L^{-1}.

Since the contents of iron in land plants was found to be 70–700 μg g^{-1} [37], the interference from a large amount of iron(III) should be eliminated. A cation-exchange minicolumn was thus installed into the flow line as shown in Fig. 1. Although the peaks slightly broadened due to the dispersion of sample zone, 100-fold excess of iron(III) was tolerable (Table 3). Although the elimination of iron was performed by using only the cation exchanger, the combination of a masking agent and cation exchanger could be achieved high selectivity [24]; the present system was used both the masking agent and the cation-exchange column.

3.6. Calibration graph

Calibration curves for molybdenum(VI) with and without the cation-exchange column were prepared under the selected conditions as shown in Table 2. The curves were linear over the range 1.0–20 ng mL^{-1} molybdenum(VI). Typical regression lines with and without column were $Abs = 0.996 \times 10^{-2} C_{Mo(VI)}$ ($R^2 = 0.998$) and $Abs = 1.21 \times 10^{-2} C_{Mo(VI)}$ ($R^2 = 0.999$), respectively, where Abs is the absorbance for peak height and $C_{Mo(VI)}$ is the concentration of molybdenum(VI) in ng mL^{-1}. Owing to broader peaks, the slope of regression line with column was lower than that without column. The detection limits (S/N = 3) with and without column were 0.5 ng mL^{-1} with a sample throughput of 15 samples h^{-1}. The reproducibility with and without column was satisfactory with relative standard deviations of 2.5 and 2.1%, respectively, for ten determinations of 10 ng mL^{-1} of molybdenum(VI).

3.7. Effect of foreign ions

The effect of foreign ions on the determination of 5.0 ng mL^{-1} molybdenum(VI) was examined by using the present flow system with the cation-exchange column. A relative error of less than ±5% was considered to be tolerable. The tolerance limits for these ions are given in Table 3. As can be seen, most of the ions did not interfere when they are present in 10-fold excess by weight. Positive interferences were observed from Cr(VI), Se(IV), Sn(II, IV) and V(IV, V) when present in 10-fold excess. Tungsten(VI) showed a positive interference when present in 2-fold excess; its interference could be suppressed by adding strontium(II) (Table 3). The levels of these ions in plant materials used as foodstuffs are usually lower than that of molybdenum.

3.8. Application

The proposed flow-system with cation-exchange column was applied to the determination of molybdenum in plant foodstuffs after the pretreatment described in Section 2. The analytical results are shown in Table 4. To check the accuracy of the present method, molybdenum in the same plant samples was determined by ICP-AES. These results are also given in Table 4. Analytical values obtained by the present method were in good agreement with those obtained by ICP-AES.

Table 4
Determination of molybdenum in plant foodstuffs.

Sample	Weight (g)	Dilution	Mo found[a] (ng mL^{-1})	Mo in sample[a] (μg g^{-1})	
				Present method	ICP-AES
Garlic	5.01	1/10	$2.3_5 \pm 0.1_2$	$0.23_4 \pm 0.01_2$	$0.22_4 \pm 0.00_2$
Laurel	3.40	1/10	$2.5_5 \pm 0.1_6$	$0.37_5 \pm 0.02_3$	$0.36_5 \pm 0.00_9$
Peanut	5.02	1/25	$3.8_7 \pm 0.0_5$	$0.96_4 \pm 0.01_1$	$0.93_2 \pm 0.00_7$
Rice	6.05	1/25	$3.6_9 \pm 0.0_4$	$0.76_2 \pm 0.01_0$	$0.78_2 \pm 0.01_0$
Soybean flour	5.01	1/200	$3.2_2 \pm 0.1_6$	$6.4_3 \pm 0.1_5$	$6.6_4 \pm 0.1_0$

[a] Average and standard deviation ($n = 3$).

4. Conclusion

A new catalytic reaction system is presented for the spectrophotometirc flow-injection determination of molybdenum(VI). The use of coupling of HBS with NED in the presence of bromate and CTA as an activator for molybdenum(VI) makes it possible to determine trace amounts of molybdenum in plant materials. The proposed procedure yields high sensitivity comparable to other procedures, as can be seen in Table 1. The interfering ions were eliminated by using a masking agent and on-line separation using minicolumn. The simplicity and reliability of the method permit the routine determination of molybdenum in plant samples.

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