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Catalytic Spectrophotometric Determination of Molybdenum

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Summary. A highly selective, sensitive, and simple catalytic method for the determination of molybdenum in natural and waste waters was developed. It is based on the catalytic effect of Mo(VI) on the oxidation of 2-aminophenol with H_2O_2. The reaction is monitored spectrophotometrically by tracing the oxidation product at 430 nm after 10 min of mixing the reagents. Addition of 800 $\mu g \cdot cm^{-3}$ *EDTA* conferred high selectivity; however, interfering effects of Au(III), Cr(III), Cr(VI), and Fe(III) had to be eliminated by a reduction and co-precipitation procedure with $SnCl_2$ and $Al(OH)_3$. Mo(VI) shows a linear calibration graph up to 11.0 $ng \cdot cm^{-3}$; the detection limit, based on the $3S_b$-criterion, is 0.10 $ng \cdot cm^{-3}$. The unique selectivity and sensitivity of the new method allowed its direct application to the determination of Mo(VI) in natural and waste waters.

Keywords. Molybdenum; Catalytic determination; 2-Aminophenol; Hydrogen peroxide; Redox reaction; Natural and waste waters.

Introduction

Determination of molybdenum as a micronutrient is receiving increased interest in environmental and biochemical studies. The US EPA drinking water health advisories recommend long-term limits of 10 $ng \cdot cm^{-3}$ for children and 50 $ng \cdot cm^{-3}$ for adults [1]. Several methods for the sensitive determination of molybdenum in natural and waste waters have been described, based on neutron activation analysis [2, 3], inductively coupled plasma mass spectrometry [4, 5], inductively coupled plasma atomic emission spectrometry [6–8], atomic absorption spectrometry [9–11], stripping voltammetry [12, 13], and high performance liquid chromatography [14, 15]. Typical detection limits are 2.5–10.0, 0.2–0.3, 0.07–8.0, 0.01–1.4, 0.34–0.5, and 0.4–4.6 $ng \cdot cm^{-3}$ of Mo(VI). However, the need for preconcentration [2–15] and relatively high costs [2–8] are common disadvantages of these methods.

Catalytic methods with spectrophotometric monitoring offer low-cost and simple alternatives for the determination of traces of elements [16–49]. Many catalytic methods for molybdenum determination are based on its effects on the oxidation of a substrate with a suitable oxidant such as ClO_3^- [18], IO_4^- [19], or

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H_2O_2 [20–33, 44, 45]. Other methods rely on its catalytic effect on the reduction of a dye with a suitable reducing agent such as NH_2NH_3Cl [34–42] or $SnCl_2$ [43]. However, poor selectivity [18, 20, 26, 27, 31–33, 37–41, 44, 45] and high detection limits [18–29, 31–45] are common disadvantages. Therefore, there is still a need for a more sensitive, selective, and precise method.

The catalytic oxidation of 0.05 *M* 2-aminophenol (**1**) with H_2O_2 in the presence of acetate buffer of *pH* = 5.0–6.0 has been used to determine Mo(VI) and W(VI) in highly pure inorganic compounds and synthetic samples [44, 45]. However, this method is characterized by its poor precision resulting from the very high blank values and the use of a completely unstable aminophenol reagent. Therefore, a thorough examination of the Mo(VI) catalyzed 2-aminophenol-H_2O_2 reaction was undertaken.

Results and Discussion

Preliminary considerations

The oxidation of **1** with H_2O_2 is a slow process that can be catalyzed by Au(III) [46], Cr(III) and Cr(VI) [47], Cu(II) [48], Mo(VI) and W(VI) [44, 45], or Nb(V) and Ta(V) [49]. The oxidation product exhibits a maximum absorbance at 430 nm and has been isolated and identified as 2-amino-3-phenoxazinone [50].

Aqueous solutions of **1**, prepared by dissolving the reagent in dilute HNO_3, HCl, or $H_2C_2O_4$ [44–46, 48, 49] are completely unstable and readily darken after preparation because of the rapid auto-oxidation catalyzed by ultra-trace amounts of ions. Therefore, sodium metabisulfite and *EDTA* were tested as stabilizing and masking agent, respectively. Preliminary experiments showed that the sensitivity of Mo(VI) determination was not affected by the presence of *EDTA* (up to 2×10^{-3} *M*) and sodium metabisulfite (up to 5×10^{-3} *M*) in the reaction cell. Therefore, several working solutions of **1** were prepared containing *EDTA* (2×10^{-3} *M*) and sodium metabisulfite (0.1–12×10^{-2} *M*). The changes in the absorbances of these solutions as a function of time were taken as measures of their stability. A solution was considered stable when its absorbance remained essentially constant for at least 24 hours. It was found that working solutions of **1** containing less than 1×10^{-2} *M* metabisulfite were completely unstable. Moreover, the solution stability increased with metabisulfite concentration, reaching its maximum above 3×10^{-2} *M* metabisulfite. To provide a stable reagent solution and to confer enhanced selectivity, the working solution of **1** was thus prepared to contain 2×10^{-3} *M EDTA* and 6×10^{-2} *M* metabisulfite, respectively; the working phosphate buffer solution contained 3×10^{-3} *M EDTA*.

The fixed time method is usually more sensitive compared with the initial rate method [16, 17]. Therefore, fixed time measurements after 10 min of mixing of the reagents was adopted in the recommended procedure to provide a reasonable sensitivity and a moderate blank reading.

Effects of reaction variables

The absorbances of the uncatalyzed reaction mixture (A_u) and of the reaction catalyzed by $10\,\mathrm{ng \cdot cm^{-3}}$ Mo(VI) (A_c) varied exponentially with *pH* in the range

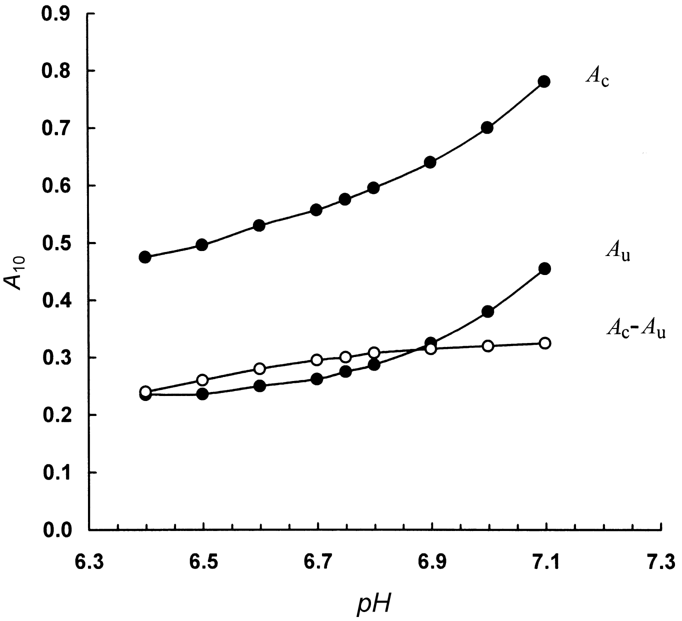

Fig. 1. Effect of *pH*; A_u: absorbance of the uncatalyzed reaction, A_c: absorbance of the reaction catalyzed by 10 ng · cm^{-3} Mo(VI); except for the abscissa, the conditions were as given in the recommended procedure

of 6.0–7.0. The sensitivity (A_c–A_u) achieved its highest values at $pH = 6.70$–7.10 (Fig. 1). Therefore, a *pH* of 6.75 ± 0.05 was adopted in the recommended procedure to provide a moderate buffering capacity and a low blank reading and to minimize the catalytic effect of Cr(VI) ions which is neglegible at $pH \geq 6.60$ [47]. The effect of buffer type at *pH* 6.75 was studied using HCl/NaOH, CH_3COOH/NaOH, glycylglycine/NaOH, *tris*-(hydroxymethyl)-aminomethane/HCl, and H_3PO_4/NaOH buffers (10 ng · cm^{-3} Mo(VI), $2.5 \times 10^{-2} M$ of the tested buffer). All of them gave an almost constant A_u value; however, A_c values of 0.433, 0.461, 0.298, 0.314, and 0.575 were observed. Therefore, phosphate buffer was used which offers enhanced sensitivity and selectivity.

The A_c values increased sharply with phosphate concentration up to $2.0 \times 10^{-2} M$; the A_u values increased gradually in the studied phosphate concentration range. The sensitivity reached an almost stable maximum in the range of 2.0–$3.0 \times 10^{-2} M$ phosphate (Fig. 2). The appearance of such a maximum is a characteristic feature for all types of activation reactions where the activator forms a ternary complex of the type activator-metal-substrate [16, 17]. Therefore, a final phosphate concentration of $2.5 \times 10^{-2} M$ was adopted in the recommended procedure in order to provide a reasonable activating effect and a buffering capacity.

The A_c and A_u values gradually increased with the concentration of **1** resulting in a maximum sensitivity in the range of 4.0–$6.0 \times 10^{-3} M$ (Fig. 3). Thus, in order to provide high sensitivity and a low reagent blank, a concentration of $4.0 \times 10^{-3} M$ of **1** was adopted in the procedure.

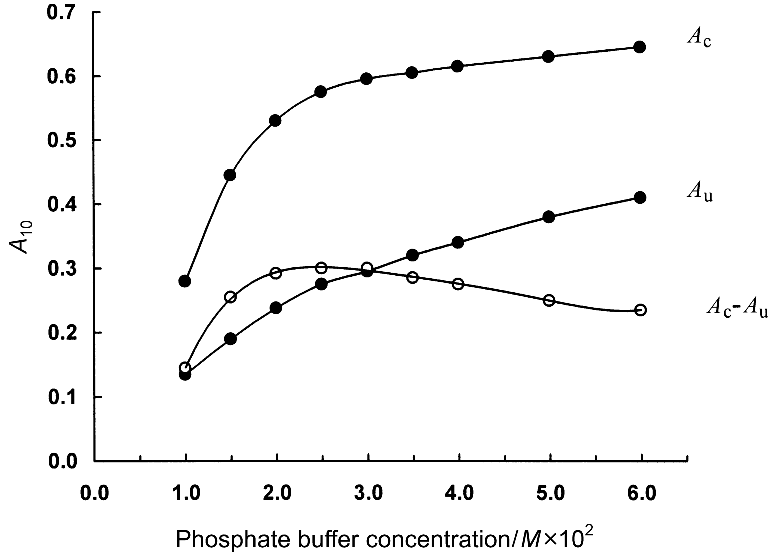

Fig. 2. Effect of phosphate buffer concentration; conditions and symbols are as given in Fig. 1

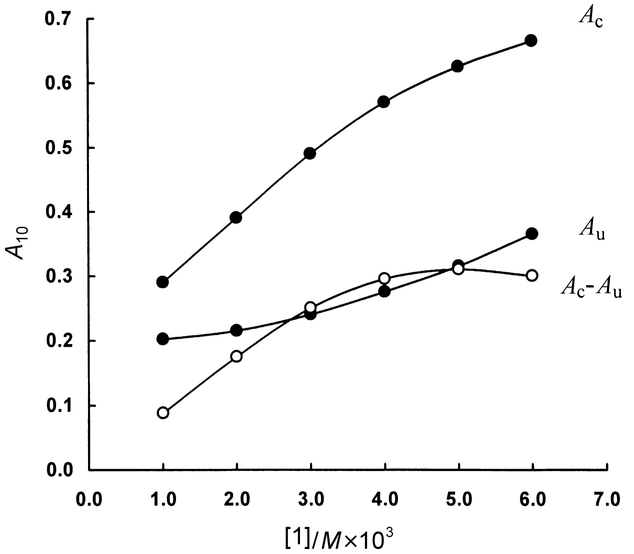

Fig. 3. Effect of the concentration of **1**; conditions and symbols are as given in Fig. 1

The absorbances A_c and A_u and the sensitivity A_c–A_u sharply increased with H_2O_2 concentration up to $2.0 \times 10^{-2}\,M$. However, they were almost independent of the H_2O_2 concentration in the range of $2.0–10.0 \times 10^{-2}\,M$. Therefore, $4.0 \times 10^{-2}\,M$ H_2O_2 were employed.

A_c and A_u increased exponentially with temperature; a working temperature of 40°C was adopted in the recommended procedure because of the moderate sensitivity and reagent blank and its convenience for operation.

The possible enhancing effects of some water-soluble solvents were tested in the determination of 5.0 ng · cm^{-3} Mo(VI) (ethanol, methanol, 2-propanol, acetonitrile, dimethylsulfoxide, dimethylformamide, 1,4-dioxane; 5–10% v/v; higher concentrations of these solvents gave low A_c and sensitivity values). The above solvents gave high A_c and A_u values, but lower sensitivity compared to that obtained in their absence. The effects of added salts was studied using suprapure $(NH_4)_2SO_4$, KCl, and $NaNO_3$. The tested salts had almost no effect on the sensitivity up to 0.2 *M*; however, both A_c and A_u very slightly increased with increasing salt concentration.

The absorbance of the catalyzed reaction was independent of the order of mixing the reagents. However, H_2O_2 was added before **1** to avoid the possible autooxidation of **1** catalyzed by Mo(VI). Moreover, A_c values were almost independent of the time of contact between Mo(VI) and H_2O_2 before the addition of **1**. For example, in the determination of 10 ng · cm^{-3} of Mo(VI), the recoveries after 1, 5, and 10 minutes of contact between Mo(VI) and H_2O_2 were 100, 99, and 97%.

The effects of 67 potential interfering species which may accompany molybdenum in natural and/or waste waters were studied using 5.0 ng · cm^{-3} Mo(VI). The maximum tolerable concentrations of these species are shown in Table 1, where the tolerance level is defined as the concentration of foreign ion that produced a change in the absorbance of the catalyzed reaction of less than 5%. Except for NO_2^-, I^-, SCN^-, Au(III), Cr(III), Cr(VI), and Fe(III), all ions tested were tolerated at reasonably high concentrations without any special precaution.

Sulfamic acid and Hg(II) effectively masked the effects of NO_2^-, I^-, and SCN^-, respectively as described in the procedure. However, *EDTA* and/or oxalate could not improve the selectivity towards ng · cm^{-3} levels of Au(III), Cr(III), Cr(VI), and

Table 1. Tolerance levels of foreign species in the determination of 5 ng · cm^{-3} Mo(VI)[a]

Tolerance level/μg · cm^{-3}	Foreign species[b]
> 500	acetate, sulfamate, *EDTA*, *CyDTA*, *NTA*, glycylglycine, *Tris*, NO_3^-, Cl^-, Br^-, ClO_4^-, HCO_3^-, SO_4^{2-}, $S_2O_5^{2-}$, Na^+, K^+, NH_4^+, Li^+
> 100	CN^-, F^-, $B_4O_7^{2-}$, Mg(II), Ca(II), As(III), As(V), Al(III), Zn(II)
50	citrate, oxalate, tartrate, Tl(I)[c], Ba(II), Cd(II)[c], Cu(II)[c], Ni(II)[c], Sr(II), Cr(III)[c]
5	NH_2NH_3Cl, NO_2^- [d], SO_3^{2-}, Ag(I)[c], Be(II), Co(II)[c], Hg(II), Pd(II), Pb(II)[c], Sn(II), Bi(III)[c], Fe(III)[c], Ce(III)[c], Hf(IV), Sn(IV), Th(IV)[c], Ti(IV)[c], Zr(IV)[c], Nb(V)[c], Ta(V)[c], U(VI), W(VI)
1	I^- [d], SCN^- [d], Fe(II)[c], V(V)[c], V(IV)[c]
0.10	Au(III)[c], Cr(VI)[c]
0.01	NO_2^-, SCN^-, S^{2-}, Fe(II), Fe(III), Cr(III), V(V), Nb(V), Ta(V), Cr(VI),

[a] Reaction conditions as given in the recommended procedure; [b] species with buffering action were adjusted to *pH* 6.75 before studying their effects; *EDTA*: ehtylenediamine tetraacetic acid disodium salt; *CyDTA*: *trans*-1,2,-diaminocyclohexane-N,N,N′,N′-tetraacetic acid; *NTA*: nitrilotriacetic acid; [c] after reduction and coprecipitation steps; [d] using sulfamic acid and/or Hg(II) masking solutions

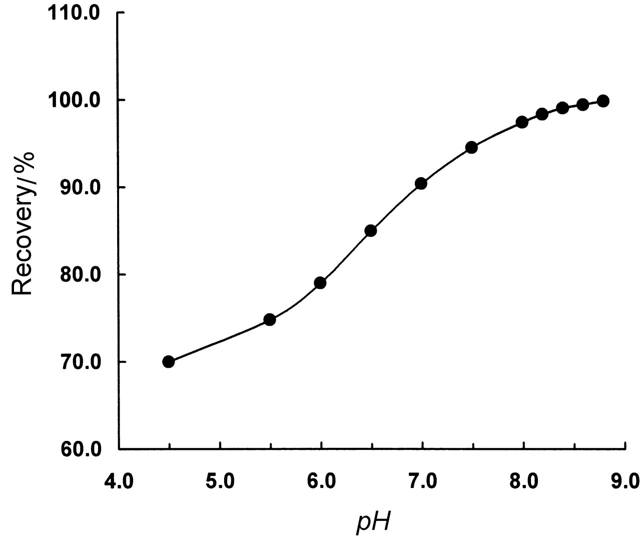

Fig. 4. Effect of *pH* of precipitation on the recovery of Mo(VI); conditions and symbols are as given in Fig. 1

Fe(III) ions. On the other hand, up to 5 $\mu g \cdot cm^{-3}$ Sn(II) had no effect on the determination of Mo(VI); however, at a 1:1 ratio it destroyed the catalytic effects of Au(III) and Cr(VI) ions. Therefore, 0.10 $\mu g \cdot cm^{-3}$ Sn(II) were added to the samples to reduce these ions. Otherwise, traces of Cr(III), Fe(II), and Fe(III) may be coprecipitated quantitatively from neutral media in presence of a collector such as Fe(III), La(III), Mn(II), or Al(III) [16]. However, Fe(III), La(III), and Mn(II) are well known to coprecipitate Mo(VI) ions [51], resulting in very poor recoveries of Mo(VI). Therefore, Al(III) was employed in the procedure as a collector due to its ability to give a quantitative and rapid coprecipitation of Cr(III) and Fe(III) ions, but not creating interferences in the analytical determination of Mo(VI) due to its high tolerance level (Table 1).

The effects of the different precipitation variables on Mo(VI) recovery were thoroughly investigated. Quantitative recoveries of Mo(VI) were obtained in the *pH* range of 8.20–8.80 in presence of 10–50 $\mu g \cdot cm^{-3}$ Al(III) (Fig. 4). At higher *pH* values, partial dissolution of the precipitate was observed. Moreover, concentrations of 10, 50, 100, 150, 200, and 250 $\mu g \cdot cm^{-3}$ Al(III) at $pH = 8.40$ gave recoveries of 100, 98.8, 96, 91, 87, and 83%. On the other hand, a salt such as $(NH_4)_2SO_4$ added during the coprecipitation step in concentrations up to 0.10 *M* had no effect on the recovery of Mo(VI). Therefore, a *pH* of 8.40±0.1 in the presence of 30 $\mu g \cdot cm^{-3}$ Al(III) was adopted in the procedure. Such a treatment successfully eliminated the interfering effects of 5 $\mu g \cdot cm^{-3}$ of Cr(III) and Fe(III) ions and 0.10 $\mu g \cdot cm^{-3}$ of Au(III) and Cr(VI) ions.

Despite of its simplicity and high sensitivity, the most interesting feature of the implemented method is its selectivity, especially towards NO_2^-, I^-, SCN^-, Cu(II), Au(III), Fe(III), Nb(V), Ta(V), Cr(III), Cr(VI), and W(VI) which are known to catalyze the 2-aminophenol-H_2O_2 reaction [44–49].

Table 2. Determination of Mo(VI) in natural, ground, and waste waters[a]

Sample[b]		Molybdenum conc.[c]/ng · cm^{-3}		Recovery/%
No.	Type	Added	Found	
1	Nile River	–	2.27±0.16	–
		4.00	6.33±0.18	101.5
2	Natural water (Siwa)	–	1.15±0.12	–
		4.00	5.06±0.08	97.8
3	Natural water (Mineral)	–	1.64±0.13	–
		4.00	5.60±0.12	99.0
4	Well water	–	2.70±0.14	–
		4.00	6.75±0.10	101.3
5	Well water	–	1.95±0.15	–
		4.00	5.88±0.15	98.3
6	Waste water	–	6.42±0.10	–
		4.00	10.54±0.11	103.0
7	Waste water	–	4.19±0.14	–
		4.00	8.08±0.12	97.3

[a] Reaction conditions as given in the recommended procedure; [b] No. 1: Nile River, downstream about 1 km from Kasar El-Nile bridge on June 21st, 2000 ($pH = 8.17$); Nos. 2 and 3: natural waters from the local market; Nos. 4 and 5: ground waters collected on June 27th, 2000 from Matrouh city; No. 4: 30°53′8.55″ N and 28°32′21.66″ E, Sawani Samalouth, $pH = 7.41$; No. 5: 31°04′14.13″ N and 28°28′10.23″ E, Saleh Gali, $pH = 7.63$; Nos. 6 and 7: waste waters collected on August 10th, 2000 from cement and steel industrial plants of Helwan, Cairo; [c] added to or found in the original sample; found = mean±standard deviation ($n = 3$)

Calibration graph and detection limit

The calibration graph prepared following the recommended procedure gave a linear relationship ($r = 0.998$) between absorbance and Mo(VI) concentration up to 11.0 ng · cm^{-3} of Mo(VI). The detection limit was determined as 0.10 ng · cm^{-3} Mo(VI) (three times the standard deviation of the blank; $3S_b$-criterion). The precision of the method was assessed by analyzing 1,5, and 10 ng · cm^{-3} Mo(VI) in aqueous solutions; it gave an average recovery of 98.7% with relative standard deviations below 1.1% ($n = 5$).

Applications

The new method was applied to the determination of Mo(VI) in Nile River water, ground water, and industrial waste waters (Table 2). Recovery experiments for the analyzed samples proceeded quantitatively with standard deviations of ±0.15 ng · cm^{-3} Mo(VI) ($n = 3$), indicating the high accuracy and precision of the technique.

Conclusions

The suitability of the 2-aminophenol-H_2O_2-Mo(VI) system allowed the development of a simple and low-cost method for molybdenum determination down to

0.10 ng · cm^{-3}, a level that is eighty times lower than that achieved by the standard ICP-AES method [6]. The simplicity, sensitivity, and freedom from most interferences are significant advantages of the method compared with the high-cost NAA, ICP-MS, and ICP-AES methods. Moreover, the procedure surpasses most kinetic methods [18–29, 31–45] for Mo(VI) determination in sensitivity and selectivity.

Experimental

Apparatus

Absorbance measurements were performed on a precalibrated Spekol-11 spectrophotometer (Germany) equipped with 50 mm matched cells. The temperature of the cell compartment of the spectrophotometer was controlled by circulating water from a PolyScience thermostatted water bath (Niles, IL, USA) with a stability of ±0.1°C. Eppendorf vary-pipettes (Westbury, NY, USA; 10–100 and 100–1000 mm^3) were used to deliver accurate volumes. Measurements of *pH* were made on a calibrated EDT (Dover, Kent, UK) *pH*-mV meter model GP 353 equipped with an EDT combined glass electrode with an accuracy of ±0.01. All glassware and storage bottles were soaked in 10% HNO_3 overnight, thoroughly rinsed with fresh distilled, deionized H_2O, and dried prior to use.

Reagents

All chemicals were of analytical reagents grade (Merck, Darmstadt, Germany; Fluka, Buchs, Switzerland). Freshly distilled de-ionized H_2O was used throughout.

A stock standard solution of 1000 μg · cm^{-3} of Mo(VI) was prepared from Na_2MoO_4. A 50 ng · cm^{-3} working standard solution was freshly prepared from the stock solution. A 2.0 *M* H_2O_2 solution was used. A 0.10 *M* working solution of 2-aminophenol (**1**) was prepared by mixing 0.545 g of the reagent with 0.6 cm^3 of suprapure HCl and dissolving in about 20 cm^3 of H_2O, followed by addition of 0.037 g of *EDTA*, 0.57 g of sodium metabisulfite, and H_2O and adjusting the *pH* to 4.0±0.2 (partial turbidity appeared at higher *pH* values). The resulting solution was diluted to 50 cm^3 in a calibrated flask which was wrapped with aluminum foil and stored at 4°C when not in use. This reagent is stable for at least one week.

A phosphate buffer solution was prepared by mixing 6.25 cm^3 of 1.0 *M* H_3PO_4 with 0.112 g *EDTA* and diluting to about 90 cm^3 with H_2O. The *pH* of this solution was adjusted to 6.75±0.02, and the solution was diluted to 100 cm^3 in a calibrated flask.

Solutions of 2% (w/v) sulfamic acid and 2 μg · cm^{-3} Hg(II) were used as masking agents for NO_2^-, I^-, and SCN^- ions. A collector solution for the coprecipitation step was prepared by dissolving 2.0 g of $AlCl_3 \cdot 6H_2O$ in a 100 cm^3 calibrated flask. A 5% (w/v) solution of NaOH was also used.

Treatment of water samples

Collected samples were filtered and acidified to $pH = 2.0 \pm 0.2$. To 70–80 cm^3 of the acidified sample, 1.0 cm^3 of the sulfamic acid solution were added. The mixture was shaken well and set aside for 5 min to decompose nitrite ions. After addition of 1 cm^3 of 10 μg · cm^{-3} Sn(II) solution, the sample was shaken to reduce Au(III) and Cr(VI) ions if present. Addition of 1.0 cm^3 of the Al(III) collector solution and adjustment of the *pH* to 8.40±0.2 using the working NaOH solution led to coagulation. The formed precipitate was filtered off and washed with three 5 cm^3 portions of H_2O. Filtrate and washings were collected, the *pH* was adjusted to 6.75±0.2, 1 cm^3 of the Hg(II) solution was added to mask I^- and SCN^- ions, and the mixture was diluted with H_2O in a 100 cm^3 calibrated flask.

Recommended procedure

Keep the working solutions, treated samples solutions, H_2O, and 20 cm^3 stoppered glass test tubes (Pyrex, grade A) at 40°C in the thermostatted water bath. To one of the test tubes, transfer ≤ 2.70 cm^3 of the treated sample or the working standard Mo(VI) solution and dilute with H_2O to 2.70 cm^3. Add 2.00 cm^3 of the phosphate buffer solution and 0.10 cm^3 of the working H_2O_2 solution. Start the reaction by adding 0.20 cm^3 of the working solution of **1**, shake, and immediately transfer a portion of the reacting mixture to the 50 mm thermostated cell of the spectrophotometer. Record the absorbance value at 430 nm after 10 min of mixing against water as a reference. The Mo(VI) concentration of the unknown sample is determined from a calibration graph, similarly prepared with the standard Mo(VI) solution.

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