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Catalytic Determination of Traces of Tellurium (IV) Using the Reduction of Lauth's Violet with Sodium Sulfide

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ABSTRACT

A simple, rapid and sensitive method has been developed for determination of traces of tellurium (IV) (7.0-120.0 ng/ml) based on it's catalytic effect on the reduction reaction of lauth's violet by sulfide ion at pH 4.2. The reaction is monitored spectrophotometrically by measuring the decrease in absorbance of lauth's viole at 600 nm by the fixed time method. The detection limit is 5.0 ng/ml and the relative standard deviation for 50.0 and 100.0 ng/ml Te (IV) is 2.5 and 1.8 % respectively. The method is free from most interferences and it was applied to determination of tellurium in water real samples.

Keywords: Tellurium determination; Catalytic; Spectrophotometry

INTRODUCTION

Tellurium is widely distributed in low concentrations in rocks. Tellurium is used primarily in alloys, to which it gives an improved quality of machinability. It is most commonly alloyed with steel, but may also be combined with copper and lead to improve their workability and to make them more resistant to vibration and fatigue. Small amounts of tellurium are used in the rubber and textile industries, primarily as catalysts. A growing application of tellurium is in electrical and electronic devices, such as photocopiers, printers, and infrared detection systems. Tellurium is widely used as semiconductors and occurs in small quantities in inorganic materials and biological samples. Tellurium aerosol irritates the eyes and the respiratory tract. The substance may cause . effects on the liver, central nervous system, abdominal pain, constipation and vomiting [1-3]. Tellurium is less toxic than selenium, but some tellurium compounds, such as hydrogen tellurides, are very toxic [4]. Therefore it is potential environmental pollutant and this increases the need for development of a rapid, sensitive and simple method for the determination of trace of tellurium. There exist different methods for determination of tellurium such as spectrophotometric methods [5, 6] hydride generation atomic fluorescence spectrometry [7-9] and stripping voltammetery [10, 11]. The drawback of some of the methods lack of sensitivity [12-16], while some others extraction by toxic organic solvents require [17-19]. The reported catalytic kinetic methods for determination of Te (IV) are quite sparse

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[20, 21, 4]. The kinetic catalytic methods have shown very promising features for determination of metal ions in ultra-trace levels [22]. These methods have proved to be a cheaper and more reliable alternative to the instrumental analyses for trace determinations [23].

In this paper we wish to report a simple, rapid and sensitive method for determination of Te (IV) based on its catalytic effects on the reduction reaction of lauth's violet with sodium sulfide at PH = 4.2.

EXPERIMENTAL

Reagents

Doubly distilled water and analytical reagent grade chemicals were used.

Tellurium (IV) stock standard solution (1000ppm) was prepared by dissolving 0.1252g TeO2 (Merck) in 10 ml of 0.1 M KOH and diluting with water to 100 ml in a volumetric flask. Working solutions were prepared by appropriate dilution with water.

A solution of lauth's violet, 3.8 10 M, was prepared by dissolving 0.010 g of lauth's violet (Merck) in 10 ml of ethanol and diluting to 100 ml in a 100-ml volumetric flask with water.

Sodium sulfide solution (0.010 M) was prepared by dissolving 0.2402 g of Na S.9H O (Merck) in water and diluting to 100 ml in a volumetric flask. This solution must be prepared daily.

Apparatus

Absorption spectra were recorded using a Shimadzu Model 160-A UV-Visb-Spectrophotometer in a 1-cm glass cell and it was used for absorbance measurements at a fixed wavelength. A thermostat bath (Gallenkamp) was used to keep the reaction temperature at 30 0.1 C. A stopwatch was used for recording the reaction time.

Procedure

The reaction was followed spectrophotometrically by monitoring the change in absorbance of the reaction mixture at 600nm by a fixed time method for the first 0.5-3.0 min from initiation of the reaction. Into a series of 10-ml volumetric flacks an appropriate amount of buffer (acetate, 0.10M, pH=4.0), 3.8×10-4 M lauth's violet and 1 ml of 1.0 μg/ml Te (IV) were added. The solution was diluted to ca. 8 ml with water. Then 0.5 ml of 0.01 M Na S was added and the solution was diluted to the mark with water and mixed well. The mixture was transferred to a 1.0cm glass cell within 30 Sec from initiation of the reaction. The decrease in absorbance was measured during the first 0.5-3.0 min from initiation of the reaction (A). Time was measured from just after the addition of the last drop of sodium sulfide. A measurement in the absence of tellurium (IV) was performed to obtain the absorption values for the uncatalyzed reaction (A). The net reaction rate was calculated from the difference between the absorbance (A - A) measured at a fixed time. All the solutions were preheated to working temperature of 30 0.1 C in a thermostat bath.

RESULTS AND DISCUSSION

Lauth's violet can be reduced by sulfide ion at a very slow rate at room temperature. We found that in the presence of trace amounts of Te(IV) as a catalyst the reaction rate is faster (figure1). The accelerating effect of tellurium has been explained by the fact in the presence of tellurium ion; [STe] ions are formed, which react much faster than sulfide ions. The tellurium liberated again reacts with sulfide ion.

There are several methods, such as fixed-time, initial rate, rate constant and variable time methods for measuring the catalytic species. Among these, the fixed time method is the most conventional and simplest, involving the measurement of A at 600nm. Figure1 shows the relationship between A and reaction time (for lauth's violet -S -Te (IV) system (a) and lauth's violet -S system (b)). The reaction can be monitored spectrophotometrically by measuring the decrease in the absorbance at 600 nm (decrease in concentration of lauth's violet) with time.

Influence of variable

To establish the optimum conditions of the reaction and maximum sensitivity, the influence of different parameters on the reaction rate were studied. The effect of important parameters, such as pH, reagents concentrations, time of reaction and temperature was investigated and optimized.

Effect of pH

The effect of pH on the catalyzed and uncatalyzed reaction was studied with 3.8 10-5 M lauth's violet, and 0.0005 M S at 30 C in the pH range of 3.0-7.0 (Figure 2). The results show that the reaction rate increases for the catalyzed and uncatalyzed reaction up to pH 7.0, but the rate of increment for the catalyzed reaction is faster in pH=4.2. In higher pH values, the sensitivity decreases. This effect is due to the fact that by increasing pH (pH> 4.2) the reduction of lauth's violet in the blank reaction is faster than catalyzed reaction. Therefore, pH of 4.2 (acetate buffer) was selected for the study.

Effect of reagents concentration

The effects of reagent concentrations on the reaction were studied.

The effect of lauth's violet concentration on the rate of reaction was studied at pH 4.2, 5.0 10-4 M S and at 30 C. Results (Figure 3) show that the both of the reaction catalyzed and uncatalyzed) rates increase with increasing lauth's violet concentration. Therefore, 5.4 10-5 M lauth's violet concentration was selected. A higher concentration of dye cannot be used due to its molar absorptivity coefficient.

The effect of sulfide concentration on the rate of reaction was studied at pH 4.2 and lauth's violet concentration of 5.4 10-5 M at 30 C. Figure 4 shows that the net reaction rate increases by increasing sulfide concentration up to 6.0 10-4 M. Higher concentrations of the reagent cause a decrease in sensitivity. This effect is due to the fact that at high concentration of sulfide ions, the reduction of lauth's violet for the uncatalyzed reaction is too fast to detect the catalytic effect of Te (IV) accurately. Thus, a sulfide concentration of 6.0 10-4 M was used for further studies.

Effect of temperature

The influence of temperature on the reaction rate was studied in the range of 10-50 C in the presence of optimum pH value and reagent concentration. An increase in the rate of catalyzed and uncatalyzed reactions, but the best sensitivity is obtained at 30°C (figure 5).

Effect of time

The reaction rate was studied in the range of 0.5-7.5 min at optimum conditions. Sensitivity increases up to 5.5 min, but at 4.0 min the reaction has good sensitivity and 4.0 min was selected.

Effect of ionic strength

The effect of ionic strength on the reaction rates for both the catalyzed and ucatalyzed reactions were investigated, the salt concentration being from 0.00 to 0.75 M using 3.0 M KNO3 solution. The results indicated that, with increase in KNO3 concentration, the rates of both catalyzed and uncatalyzed reactions decrease.

Calibration Graph

The calibration graph was obtained under the optimum working condition at 600 nm using the fixed-time method. Measurements were recorded after 4.0 min from initiation of the reaction; because it provided the best regression and sensitivity and reaction time. Under the optimum conditions described above, Te (IV) can be determined in the concentration range of 7.0-120.0 ng/ml: the following regression equation was obtained; A=0.007+0.0052C Te(IV) (r=0.9978, n=8, and Sb=9.23 10-3).

The relative standard deviation for ten replicate determinations of 50 and 100ng/ml Te(IV) were 2.5% and 1.8%, respectively. The experimental limit of detection is 5.0 ng/ml Te(IV).

Effect of foreign ions

The influence of foreign ions on the system was examined with 100ng/ml Te (IV).. The tolerated limits for the ions assayed are shown in Table 1 (with relative errors less than 5%). As can be seen, most ions used have no considerable effect on the determination of tellurium (IV), even when present in 100-1000-fold excess over tellurium. However, as it was predicted, the presence of cations which form insoluble precipitates with sulfide ion would interfere the determination of tellurium (IV). These cations can be successfully removed from the solution by passing it through a column containing a cation exchanger in the form of H+. The results show that the method is relatively selective for tellurium determination.

Analysis of Real Sample

The method was applied for determination of tellurium in a sample of under ground water, aqueduct water and synthetic samples. The samples were analyzed by the method of standard addition. Table 2 shows the results of analysis of two real samples. Recovery tests for the analyzed samples were satisfactory with relative standard deviations of 3.7 %.

Table 1. Effect of foreign ions on the determination of Te(IV)

Species	(ppm_i/ppm_{Te})
Na^+, K^+, Li^+, NH_4^+, Ca^{2+}, I^-, SO_4^{2-}, Cl^-, Br^-, CO_3^{2-}, $C_2O_4^{2-}$, NO^{3-}	>1000
Mn^{2+}	500
Cr^{3+}, $S_2O_3^{2-}$, BrO_3^-, Ba^{2+}, $CH3COO^-$	100
Cd^{2+}, Cu^{2+}, Ag^{1+}, Pb^{2+}, Ni^{2+}, Se^{4+}, Hg^{2+}	Interfere

CONCLUSION

A kenetic-specrophotometric method is proposed for trace amounts of tellurium. The method is simple, highly sensitive, inexpensive and rapid, and was used for the determination of tellurium in water samples.

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Table 2. Determination of tellurium in real samples and synthetic samples

Sample	Tellurium found, ng/ml	*RSD (%)*
Well water	1.70*	-----
Aqueduct water	22.0	3.7

RSD, relative standard deviation for n=6.

- It is lowest than detection limit. Thus there isn't tellurium in this sample.

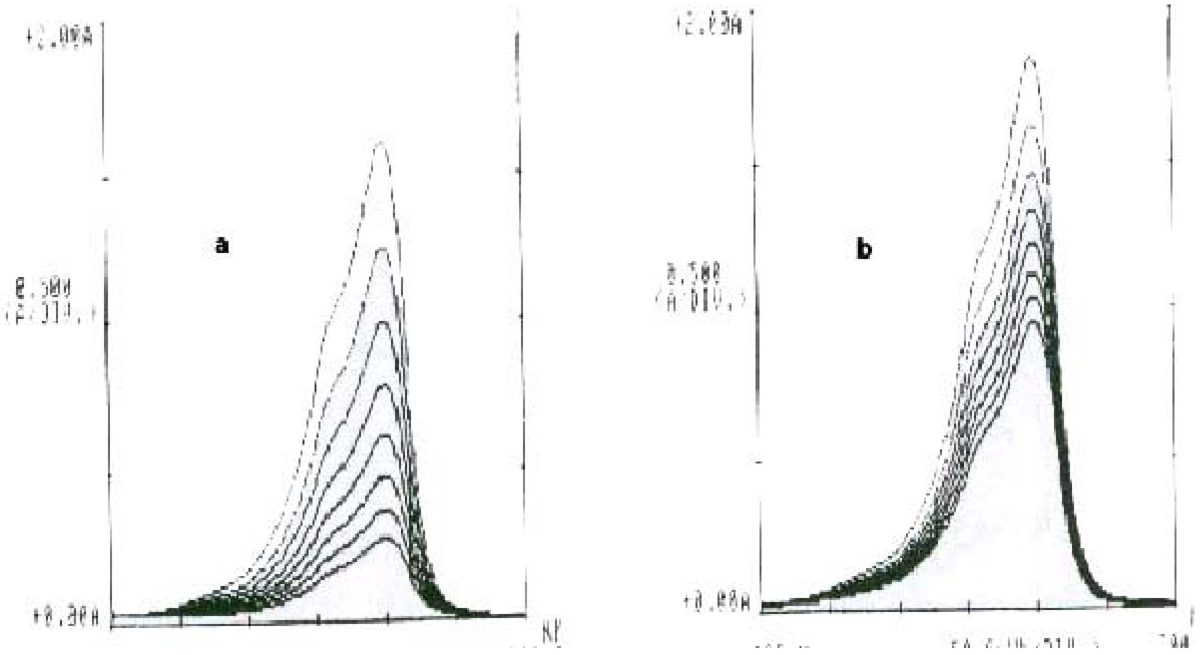

Fig.1. a: Variation of the lauth's violet-S^{2-} Te (IV)with time. b: without Te(IV). Conditions: pH, 4.2, lauth's violet 5.4×10^{-5} M, Sulfide 6.0×10^{-4} (a: 100 ng/ml Te(IV), at 30 °C .

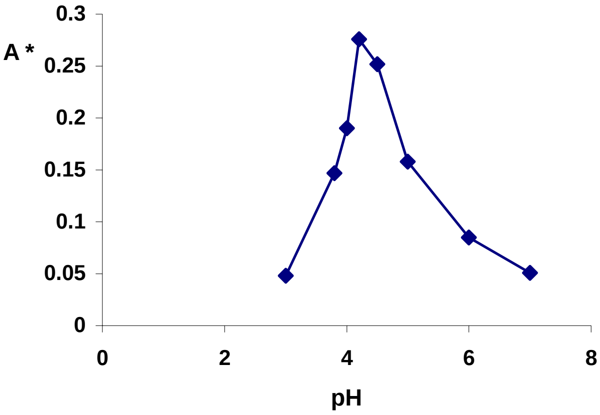

Fig.2. Effect of pH on sensitivity. Conditions: lauth's violet 5.4 10-5 M, Sulfide 5.0 10-4M, 100 ng/ml Te(IV), at 30° C.

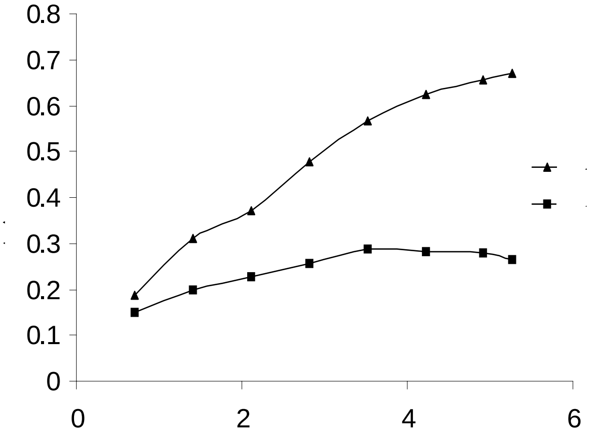

Fig.3. Effect of lauth's violet concentration. Conditions: pH, 4.2, 5.0 10-4M, 100 ng/ml Te(IV), at 30° C.

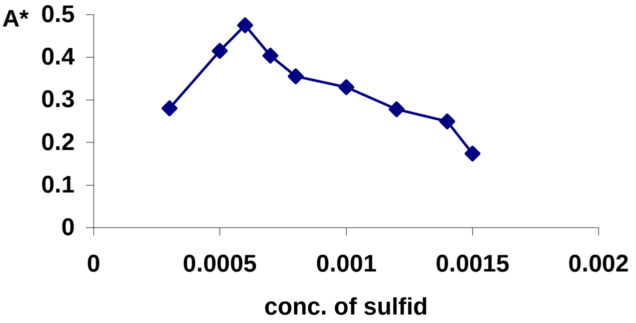

Fig.4. Effect of sulfide concentration. Conditions: pH, 4.2, lauth's violet5.4 10-5M,100 ng/ml Te(IV),at30°C.

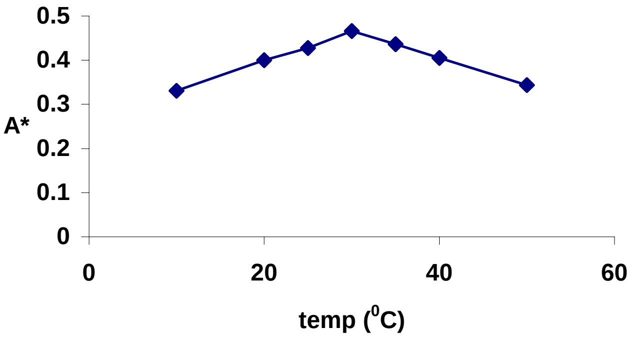

Fig.5. Effect of temperature on reaction. Conditions: pH, 4.2, lauth's violet 5.4 10-5 M, Sulfide6.0 10-4 M, 100 ng/ml Te(IV).

REFERENCES

1. K. W. Bagnall, "The Chemistry of Selenium, Telurium and Polonium", Now- York 1966.
2. I. I. Nazarenko and A. N. Ermakov, "Analytical Chemistry of Selenium and Tellurium", Halstead Press, Now- York (1972).
3. P. R. Prasad, J. D. Kumar, B. K. Priya, P. S. Ubrahmanyam, S. Ramanaiah, P. Chiranjeevi, E-Journal of Chemistry, 2007, 4, 354.
4. E. A. Cerwenka and W. C. Cooper, Arch. Environ. Health, 1961, 3,189.
5. A.A. Ensafi, M. Keyvanfard, Intern. J. Environ. Anal. Chim. 2003, 83(5), 397.
6. A. Ramesh and M. S. Subramanian, Bull. Chem. Soc. Jap, 1998, 71, 1025.
7. J.Ha, H. W. Sun, J. M. Sun, D. Q. Zhang, L. L. Yang, Anal. Chim. Acta, 2001, 448, 145.
8. K. Marcucci, R. Zamboni and P. D,Ulivo, Spectrochim. Acta. Part B, 2001, 56, 393.
9. P. C. Montensinos, M. L. Cervera, A.Pastor, M. D. L.Guardia, Anal. Chim. Acta, 2003, 481, 291.
10. T. Ferri, S. Rossi and P. Sangiorgio, Anal. Chim. Acta. 1998, 361, 113.
11. L. Li, P. He, Y. Fang, J. Fresenius, Anal. Chem., 2000, 366, 239.
12. S.B. Khoo, R. Ye, Anal. Chim. Acta, 2002, 453, 209.

13. K. H. Desai, Y. K.Agraval, Anal. Lett., 1987, 20, 11.
14. E. A.Terpinski, Analyst, 1988, 113, 1473.
15. A. S. Amin and M. N. Zareh, Anal. Lett., 1996, 29, 2177.
16. Y. Y. Zhu, Q. H. He and J. N.Qian, Lihua Jianyan, Huaxue Fence, 1996, 32, 11.
17. P. P. Kish, I. S. Balog, V. A. Andrukh, and M. G. Golomb, Zh. Anal. Khim., 1990, 45, 915.
18. V. G. Skripchuk, Zh. Anal. Khim, 1981, 36, 1362.
19. V. G. Skripchuk, O. N. Chupakhim, V. N. Charushin and N. I. Ostyakaova, Zh. Anal. Khim., 1982, 37, 49 .
20. P. Safavi, A, Afkhami and A. Massoumi, Microchem. J., 1995, 52, 3.
21. M. Shamsipur and M. F. Mousavi, Iranin J. Chem & Chem. Eng., 1995, 14, 1.
22. H. A. Mottola, “Kinetic Aspects of Analytical Chemistry in Chemical Analysis”, Vol. 96 (J. D. Wineforrdner, Ed.), Wiley Interscience, New Yourk 1988.
23. K. B. Yatsimirskii, Kinetic methods of analysis, Pergamon Press, London. . 1966.