Visual Detection of Arsenic Using Hydride Generation Followed by Reaction with Silver Bis(2-ethylhexyl)dithiocarbamate Retained in a Support Filter

Yoshito WAKUI[†] and Toshishige M. SUZUKI

Research Center for Compact Chemical System, National Institute of Advanced Industrial Science and Technology (AIST), 4-2-1 Nigatake, Sendai, Miyagi 983-0036, Japan

In this study, a simple and effective method for the detection of trace amounts of arsenic in water samples was developed. Arsenic hydride generated by the reduction of a water sample was passed through a sensing filter retaining silver bis(2-ethylhexyl)dithiocarbamate complex. The original yellow color of the filter immediately turned reddish violet. The difference of color was observed by a reflection spectrophotometer. Sensing filters made of glass fiber gave the highest sensitivity. Addition of low volatile amines effectively stabilized the performance of the sensing filter. Common anions including phosphate ion did not interfere with the arsenic detection. Visual detection of 10 $\mu\text{g dm}^{-3}$ was achieved in $\phi 10$ mm filter area using 60 cm^3 of sample solution.

Keywords Arsenic, visual detection, hydride generation, silver dithiocarbamate

(Received February 26, 2014; Accepted April 22, 2014; Published June 10, 2014)

Introduction

A simple yet highly sensitive detection method for trace arsenic is needed for on-site and real time monitoring of environmental, industrial and drinking waters. Some portable systems have been developed for field analysis of arsenic.¹ Among them, the Gutzeit method, which uses hydride generation and reaction with mercury salts, enables visual detection of arsenic with high sensitivity and selectivity.^{2,3} This method was applied for commercial survey kits. But the utilization of toxic mercury compound is becoming unfavorable recently. Spectrophotometric measurements were attempted by using various reagents like iodide,⁴ 8-mercaptoquinoline,⁵ Ferrozine,⁶ Bismuthiol II,⁷ Ethyl Violet,⁸ Rhodamine B,⁹ and Azure B,¹⁰ but their sensitivity or selectivity were insufficient. The molybdenum blue method¹¹⁻¹³ has been extensively used in the colorimetric analysis of arsenic due to the strong absorption band of reduced heteropolyacids, and was applied for naked-eye detection.¹⁴ However the principal problem of the Mo-blue method is strong interference from coexisting ions, especially from phosphate. Although methods to use molybdoarsenate and dyes exhibited high sensitivity,¹⁵⁻¹⁷ the procedures are still complicated. Visual detection of arsenic hydride using auric chloride as a color-developing agent was reported,¹⁸ but the gold solution revealed limited stability. As an alternative method, arsenic hydride was trapped in an organic solution of silver diethyldithiocarbamate (Ag(DDTC)) and was accompanied by a characteristic color change of the solution. This phenomenon was applied to colorimetric determination of arsenic in actual samples.^{19,20}

When the silver dithiocarbamate complex is stably retained on a filter support, a simple sensing filter that is selective for

arsenic can be fabricated. In this study, we chose the liquid extractant bis(2-ethylhexyl)ammonium bis(2-ethylhexyl)dithiocarbamate (BBDC) for the synthesis of silver bis(2-ethylhexyl)dithiocarbamate (Ag(BDC)) complex. Bis(2-ethylhexyl)dithiocarbamate is known to form a stable metal complex,²¹⁻²⁴ and is also used for the selective separation of heavy metals. In our work, prepared Ag(BDC) was stably retained in the filter supports and worked as a signaling reagent for arsenic hydride. In fact, a reddish violet color developed immediately when the gaseous arsenic hydride was passed through the sensing filter. Several kinds of filter supports were examined in order to obtain high sensitivity by marked color change. Addition of low volatile amines was essentially required to maintain the life of sensing filters. Influence of diverse ions including phosphate ion was checked. Naked-eye detection of less than 100 $\mu\text{g dm}^{-3}$ range was demonstrated.

Experimental

Reagents and chemicals

For synthesis of BBDC, we referred to our previous report.²⁴ In a stoppered test tube, 25 mmol of bis(2-ethylhexyl)amine ((2EH)₂NH) and 12.5 mmol of carbon disulfide were stirred overnight at 30°C under argon. The derived viscous pale yellow liquid, BBDC, was degassed under reduced pressure, and was analyzed with ¹H NMR, ¹³C NMR and infrared spectrophotometry. The yield was evaluated as >90% by integrating the NMR peaks. The heptane solution containing 0.02 M (M = mol dm⁻³) BBDC was shaken for 30 min with 0.02 M silver acetate solution at pH 4 buffered by 0.05 M acetate.²⁵ After centrifuging, the organic phase was washed with 0.01 M nitric acid and water successively, then used for the impregnation into filter supports. In case additional amine was incorporated in filters as a stabilizer, the 1 M amine solution in

[†] To whom correspondence should be addressed.
E-mail: y-wakui@aist.go.jp

heptane was mixed with the Ag(BDC) solution to achieve the same concentration as the silver complex.

The solutions of arsenic were prepared by diluting commercial standard solutions of arsenic(III) (Wako, 1 g dm⁻³), and those of other ions were prepared in a similar manner. Zinc powder was of arsenic analysis grade (Wako, particle size < 75 µm), and the other chemicals were of guaranteed grade.

Apparatus

Arsenic and silver concentrations were measured by ICP-optical emission spectrophotometer (ICP-OES, SII SPS3100). The color of filters was measured by reflection spectrophotometer (Konica Minolta CM-2600D), and was digitized in CIE *L*a*b** color scale.^{26,27} The color difference ($\Delta E^*(ab)$) before and after the reaction was derived as follows:

$$\Delta E^*(ab) = ((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2}. \quad (1)$$

Procedures

The heptane solution containing Ag(BDC) was uniformly dropped on a $\phi 25$ mm filter, then dried in air for 30 min. To block trace hydrogen sulfide possibly contained in the gas flow, zinc acetate paper was used, which was prepared by dipping a filter paper in 0.25 M zinc acetate solution and dried in air. The zinc acetate paper, a spacer, and a sensing filter were enclosed in a filter holder (Fig. S1, Supporting Information).

The conventional zinc-hydrochloric acid method was used for the generation of arsenic hydride from a sample solution.^{28,29} To the sample solution in a 100-cm³ conical flask, hydrochloric acid was added so that the final concentration reached [HCl] = 1.0 – 1.5 M. Then 5 cm³ of 0.18 M tin(II) chloride solution was added and the mixture was kept for 15 min. Immediately after addition of zinc powder (3.0 g), the filter holder was connected to the end of a conical flask. Arsenic hydride and hydrogen gas evolved were passed through the filter induced by spontaneous pressure. After 1 h of reaction, the reflection spectrum was measured at the center of the filter, and visual detection could be carried out by comparing the color with the standard color chart. By using a larger volume of a sample solution, higher sensitivity was expected. But a large amount of acid would be needed. As such, 20 and 60 cm³ were selected as the practically appropriate volume. A masking sheet of $\phi 10$ mm was inserted between the zinc acetate paper and the sensing filter in order to gain more intense color contrast by narrowing the filtration area.

Results and Discussion

The extractant, BBDC, was composed of an ionic pair ($R_2NH_2^+$ and $R_2NCS_2^-$ (BDC)), where R is a 2-ethylhexyl group. When 0.02 M BBDC heptane solution was shaken with excess aqueous silver solution, the molar ratio of extracted silver to BBDC was 1.00 ± 0.03 ($n = 5$). Consequently, BBDC was proved to extract silver quantitatively by forming a 1:1 complex³⁰ as expressed in Eq. (2),

where o denotes the species in an organic phase. The equimolar mixture of Ag(BDC) and $(2EH)_2NH$ was expected to be retained in filter supports. A cellulose filter retaining 0.4 µmol cm⁻² of Ag(BDC) was prepared, and the reflection spectrum was monitored in air at room temperature. The absorbance at

Table 1 Effect of the properties of supporting filters on color development

Material Type ^a	Cellulose							Cellulose acetate	Glass fiber
	2 (A)	3 (W)	4A (A)	5A (A)	5B (A)	5C (A)	541 (W)	C300A (A)	GA-100 (A)
Grade/µm	5	6	1	7	4	1	22	3	1
Thickness/mm	0.26	0.39	0.12	0.22	0.21	0.22	0.16	0.135	0.44
Hydrogen Permeability ^b	62	19	7	70	32	12	97	8	46
$\Delta E^*(ab)$	18	18	1	25	6	1	12	12	30

As: 0.1 mg dm⁻³, 20 cm³. Filter: $\phi 25$ mm.

a. (A): Advantec, (W): Whatman. b. (STD)cm³ min⁻¹ hPa⁻¹ cm⁻².

360 nm remained at almost a constant value during the 90 days, i.e., 0.83 ± 0.03 . This showed the complex Ag(BDC) maintained high stability in air in an ambient environment. With the addition of zinc powder, arsenic hydride was generated immediately accompanied by hydrogen gas. According to the ICP-OES analysis, approximately 97% of arsenic was liberated as the hydride from the sample solution containing 0.2 mg of arsenic within 10 min (Fig. S2, Supporting Information). When a sensing filter was connected to the flask end, the initial pale yellow color rapidly changed to reddish violet due to the reaction with arsenic hydride. The reflection spectra and color difference were measured with a reflection spectrophotometer. When 60 cm³ of 0 – 100 µg dm⁻³ arsenic solutions were applied, the peak intensity at around 510 – 540 nm increased (Fig. S3, Supporting Information) as has been observed in Ag(DDTC) methods in solution.^{19,20} The stability of the developed color was measured by leaving the reacted filter in air at room temperature. The initial $\Delta E^*(ab)$ value, 23.9, became 22.9 (–4.4%) after 6 h, and the change was almost unrecognized visually. Consequently, this sensing system was considered to have sufficient stability for actual detection of arsenic.

Various filter supports were examined to prepare sensing filters, and the color difference values ($\Delta E^*(ab)$) are listed in Table 1 along with their hydrogen permeability property. Filter paper having higher hydrogen permeability like 5A showed large $\Delta E^*(ab)$ values. On the other hand, for those having low permeability like 4A and 5C, the color change was quite limited and could barely be detected by the naked eye. Filter 541 showed low sensitivity in spite of its quite high permeability, probably due to the lack of contact time caused by the large pore size and thinness. Among the tested supports, glass fiber filter GA-100 with considerable thickness and moderate permeability exhibited the maximum color change, and was thus chosen as the support. Color change for 0.1 mg dm⁻³ arsenic solution was measured by varying the amount of Ag(BDC) from 0.2 to 8.2 µmol cm⁻². The observed $\Delta E^*(ab)$ values increased with the amount of loading up to 2.0 µmol cm⁻² but it became constant at higher amounts. Therefore the loading of Ag(BDC) was fixed at 2.0 µmol cm⁻² thereafter.

A decrease in sensitivity was sometimes observed when the newly prepared filters were left to stand in air for several days. Such deterioration occurred accompanied by the weight loss and was hence thought to be caused by the loss of free amine from a filter. Free amine is assumed to work as the reaction medium between arsenic hydride and Ag(BDC) in the sensing filter. In order to suppress the loss of sensitivity, low volatile amines, tri-*n*-decylamine ((C₁₀)₃N) or tridodecylamine (mixture of

isomers, $(C_{12})_3N$), were added to be equimolar to $Ag(BDC)$. The relationship between the color change ($\Delta E^*(ab)$) and the time left standing after preparation is exhibited in Fig. 1. Obviously, the addition of low volatile $(C_{10})_3N$ and $(C_{12})_3N$ maintained high sensitivity for a longer time than $(2EH)_2N$. Therefore, $(C_{10})_3N$ was added to filters after this experiment.

Interference from coexisting ions was examined by mixing 0.1 mg dm^{-3} of arsenic and 100 times (10 mg dm^{-3}) of another ion. The difference of $\Delta E^*(ab)$ values between the presence and absence of a coexisting ion is exhibited in Table 2. Most ions except $Se(IV)$ and $Sb(III)$ showed little difference in values, indicating the color change was hardly recognized visually. Dark black coloring by $Se(IV)$ and dark red by $Sb(III)$ suggested hydride formation and reaction with $Ag(BDC)$.^{31–33} Using 60 cm^3 of solutions of various arsenic concentrations, the derived $\Delta E^*(ab)$ values were plotted in Fig. 2. Measurement errors by the spectrophotometer were 29, 27, 22 and 13% at 5, 10, 50 and $100 \text{ } \mu\text{g dm}^{-3}$, respectively, and the detection limit was estimated to be around $3 \text{ } \mu\text{g dm}^{-3}$, derived from blank signals. The color change of the filter was not clearly recognized at less than $5 \text{ } \mu\text{g dm}^{-3}$, hence this was determined to be the detection limit under the experimental conditions. The difference of colorations was visually distinguishable between 5 and $10 \text{ } \mu\text{g dm}^{-3}$, while the resolution of color decreased at the higher region as shown in Fig. 2. An arsenic concentration of 0.01 mg dm^{-3} (10 ppb) showed $\Delta E^*(ab) = 11$, and was clearly detected by the naked eye (Fig. 3). This result shows that the sensing filter has the potential for use in the examination of drinking water according to the official guidelines of the World Health Organization³⁴ and US Environmental Protection

Agency.³⁵

Acknowledgements

This work was supported by JSPS KAKENHI Grant No. 25281038.

Fig. 2 Relationship between arsenic concentration and the color difference.

Arsenic solution: 60 cm^3 . Filter area: $\phi 10 \text{ mm}$.

Fig. 1 The effect of additive amines on the color difference.

○: $(C_{10})_3N$, □: $(C_{12})_3N$, △: $(2EH)_2NH$, ●: none.

Arsenic solution: 0.1 mg dm^{-3} , 20 cm^3 . Filter area: $\phi 25 \text{ mm}$.

Fig. 3 Photograph of color developed filters.

Arsenic solution: 60 cm^3 . Filters with $\phi 10 \text{ mm}$ mask.

Table 2 Interference from coexisting ions on color development by arsenic hydride

Ion	Al(III)	Bromide	Ca(II)	Cd(II)	Cu(II)	Fe(III)	Mn(II)	Mo(VI)
$\Delta(\Delta E^*(ab))^a$	−1.8	0.5	−1.7	0.6	−1.6	1.7	−0.4	−0.1
Ion	Pb(II)	phosphate	Se(IV)	Sb(III)	V(V)	Y(III)	Zr(IV)	
$\Delta(\Delta E^*(ab))^a$	3.1	−0.2	31.5	13.8	−0.2	−0.1	−1.7	

As: 0.1 mg dm^{-3} , other ions: 10 mg dm^{-3} , 20 cm^3 . Filter: $\phi 25 \text{ mm}$.

a. $\Delta(\Delta E^*(ab)) = \Delta E^*(ab)(As + \text{coexisting ion}) - \Delta E^*(ab)(\text{only As})$.

Supporting Information

This information includes: apparatus to detect arsenic hydride, time dependency of evolution of arsenic hydride and hydrogen, and absorbance spectra of color developed filters. This material is available free of charge on the Web at <http://www.jsac.or.jp/analsci/>.

References

1. D. Melamed, *Anal. Chim. Acta*, **2005**, 532, 1.
2. J. W. Barnes and C. W. Murray, *Ind. Eng. Chem., Anal. Ed.*, **1930**, 2, 29.
3. J. Cherukuri and Y. Anjaneyulu, *Int. J. Environ. Res. Public Health*, **2005**, 2, 322.
4. K. Tanaka and N. Takagi, *Anal. Chim. Acta*, **1969**, 48, 357.
5. V. Stará and J. Starý, *Talanta*, **1970**, 17, 341.
6. G. J. Kellen and B. Jaselskis, *Anal. Chem.*, **1976**, 48, 1538.
7. T. Minami, Y. Yamamoto, and S. Ueda, *Bunseki Kagaku*, **1978**, 27, 419.
8. H. W. Gao, *Talanta*, **1995**, 42, 891.
9. A. Pillai, G. Sunita, and V. K. Gupta, *Anal. Chim. Acta*, **2000**, 408, 111.
10. T. Cherian and B. Narayana, *Anal. Lett.*, **2005**, 38, 2207.
11. T. Kiba and M. Ura, *Nippon Kagaku Zasshi*, **1955**, 76, 520.
12. D. B. Dubovik, T. I. Tikhomirova, A. V. Ivanov, P. N. Nesterenko, and O. A. Shpigun, *J. Anal. Chem.*, **2003**, 58, 802.
13. S. Tsang, F. Phu, M. M. Baum, and G. A. Poskrebyshev, *Talanta*, **2007**, 71, 1560.
14. H. Matsunaga, C. Kanno, and T. M. Suzuki, *Talanta*, **2005**, 66, 1287.
15. S. Motomizu, T. Wakimoto, and K. Tōei, *Bunseki Kagaku*, **1982**, 31, 717.
16. C. Matsubara, Y. Yamamoto, and K. Takamura, *Analyst*, **1987**, 112, 1257.
17. K. Morita and E. Kaneko, *Anal. Chem.*, **2006**, 78, 7682.
18. A. Baghel, B. Singh, P. Pandey, and K. Sekhar, *Anal. Sci.*, **2007**, 23, 135.
19. T. Kaneshige, M. Takizawa, and H. Nagai, *Bunseki Kagaku*, **1964**, 13, 780.
20. A. G. Howard and M. H. Arbab-Zavar, *Analyst*[London], **1980**, 105, 338.
21. R. Diouf, S. A. Ndiaye, and L. Muhr, *Int. J. Phys. Sci.*, **2011**, 6, 3263.
22. I. Fall, M. Diaw, S. A. Ndiaye, R. N. Mendoza, M. A. Rodriguez, and T. I. S. Medina, *Bull. Chem. Soc. Ethiop.*, **1999**, 13, 105.
23. K. Musha, N. Teramae, S. Yamazaki, S. Toda, and S. Tanaka, *Nippon Kagaku Kaishi*, **1984**, 12, 1889.
24. Y. Wakui, S. A. Ndiaye, H. Matsunaga, T. Yokoyama, and K. Akiba, *Anal. Sci.*, **1998**, 14, 299.
25. Y. Shijo, E. Yoshimoto, T. Kitamura, H. Ono, N. Uehara, and T. Shimizu, *Anal. Sci.*, **1996**, 12, 959.
26. JIS Z 8730, "Colour specification—Colour differences of object colours", **2009**, Japanese Industrial Standards Committee, Tokyo.
27. M. M. Rahman, K. Fujinaga, Y. Seike, and M. Okumura, *Anal. Sci.*, **2004**, 20, 165.
28. JIS K 0101, "Testing methods for industrial water", **1957**, Japanese Industrial Standards Committee, Tokyo.
29. JIS M 8132, "Ores—Methods for determination of arsenic", **1992**, Japanese Industrial Standards Committee, Tokyo.
30. A. Hulanicki, *Talanta*, **1967**, 14, 1371.
31. A. R. Kumar and P. Riyazuddin, *Int. J. Environ. Anal. Chem.*, **2007**, 87, 469.
32. M. J. Nash, J. E. Maskall, and S. J. Hill, *J. Environ. Monit.*, **2000**, 2, 97.
33. X. Dauchy, M. Potin-Gautier, A. Astruc, and M. Astruc, *Fresenius' J. Anal. Chem.*, **1994**, 348, 792.
34. World Health Organization, "Arsenic in drinking-water: background document for development of WHO guidelines for drinking-water quality", **2003**, Geneva, <http://www.who.int/iris/handle/10665/75375>.
35. United States Environmental Protection Agency, "2011 Edition of the Drinking Water Standards and Health Advisories", **2011**, Washington, D.C.