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Luminol Chemiluminescence with Heteropoly Acids and its Application to the Determination of Arsenate, Germanate, Phosphate and Silicate by Ion Chromatography

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A flow-injection chemiluminescence (CL) method has been proposed for sensitive determination of arsenate, germanate, phosphate and silicate, after separation by ion chromatography (IC). The post-column detection system involved formation of heteropoly acid in a H_2SO_4 medium before the CL reaction with luminol in an NaOH medium. For separation, heteropoly acid formation and the CL detection reaction, pH requirements were not compatible. When present as a heteropoly acid complex with molybdenum(VI), germanium(IV) and silicon(IV) caused CL emission from oxidation of luminol, and such a CL oxidation of luminol was observed analogously for arsenic(V) and phosphorus(V) but with the addition of metavanadate ion to the acid solution of molybdate. Good sensitivity for the three analytes arsenic(V), germanium(IV) and phosphorus(V) could be given by a single set of reagent conditions, chosen carefully. Another set was suitable for determining phosphorus(V) and silicon(IV). The minimum detectable concentrations of arsenic(V), germanium(IV), phosphorus(V) and silicon(IV) were 10, 50, 1 and 10 $\mu g\,l^{-1}$, respectively. Linear calibrations for arsenic(V), germanium(IV), phosphorus(V) and silicon(IV) were established over the respective concentration ranges of 10–1000, 50–25000, 1–1000 and 50–10000 $\mu g\,l^{-1}$. The proposed IC–CL method was successfully applied to analyses of a seaweed reference material, rice wine and water samples.

Keywords: chemiluminescence; ion chromatography; luminol; heteropoly acid; arsenic(V); germanium(IV); phosphorus(V); silicon(IV)

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INTRODUCTION

For the determination of the oxoanions of arsenic(V), germanium(IV), phosphorus(V) and silicon(IV), a spectrophotometric method based on the formation of Molybdenum Blue has been applied.[1] As the flow-injection (FI) operation has a great advantage with respect to rapidity and reproducibility of determination, the development of on-line detection techniques has received considerable interest since the advent of FI analysis.[2] Spectrophotometric detection based on the Molybdenum Blue reaction has been exploited for FI determination of these oxoanions.[3–5] However, these oxoanions all react in the same manner and thus the methods lack selectivity. The simultaneous presence of arsenate and the other oxoanions, such as phosphate, in natural samples has given rise to the development of spectrophotometric methods combined with chromatographic separation techniques.[6–10]

With the aim of improving sensitivity of determination, the use of the chemiluminescence (CL) reactions of luminol oxidation is interesting, because the major advantage of CL reactions is that they usually permit determination of analytes with low detection limit.[11–13] In addition, CL reactions can be monitored without difficulty by using a sensitive light-detecting

device only. Therefore, CL has been used for the FI determination of various inorganic substances, in the FI–CL manifold on-line separation by ion chromatography (IC) has been included when necessary.[14–16] However, many inorganic anions do not cause luminol CL. This has limited applications of CL methods to anion determination by FI.[3] It is therefore necessary to turn the anions into a form active in the CL reaction. In the FI method or with IC, use of detection via luminol reactions with molecular acids has been reported recently for oxoanions which were readily converted into undissociated molecular acids on acidification.[17–19] However, CL analysis was fairly specific towards silicate, with a detection limit of 0.1 $\mu g\ l^{-1}$.[19]

In early work on the determination of the oxoanions of arsenic(V),[20] germanium(IV),[21] phosphorus(V)[22,23] and silicon(IV)[22,23] based on the luminol CL reaction with the heteropoly acid compounds of the oxoanions, batch CL measurements have been reported. However, the procedure is unsuitable for reproducible monitoring because of the fast CL reaction of luminol.[2,15] Before the final CL reaction with luminol, the reaction mixtures of the oxoanions with molybdate solutions were allowed to stand for a relatively long period of time, e.g. 5 min for phosphorus(V) and 10 min for silicon(IV).[22] Thus, the heteropoly acid–luminol CL system was likely to be unsuitable as a detector used in flow systems. In addition, the kinetics of the heteropoly acid CL reactions are more complicated and more reagents are needed, and there may be the disadvantage of requiring the addition of post-column pumps, and also the difficulty of ensuring correct operation of the post-column system in its application to an IC–CL method. Also, incompatibility of separation conditions and post-column reaction conditions may become a problem. However, the advantage of derivatization by molybdate is that ions may be detected which cannot be detected directly based on the luminol reaction, and thus seems to outweigh the disadvantages. CL detection following derivatization by molybdate has never been applied to FI analysis or IC.

By careful choice of reaction conditions in this work, one combined or mixed reagent for heteropoly acid formation (consisting of ammonium molybdate, ammonium metavanadate and sulphuric acid) was found to be suitable for determining arsenic(V), germanium(IV) and phosphorus(V) based on the luminol CL reaction, and the suitability of another set of reagent conditions was indicated for the CL determination of silicon(IV). For phosphorus(V), the latter set of reagent conditions also gave good sensitivity, comparable with that given by the former set. For the determination of arsenic(V), germanium(IV) and phosphorus(V) by IC, therefore, the existence of a single set of reagent conditions allowed us to develop a simpler and sensitive post-column detection system. Only two post-column reagent additions are made. The first addition is the reagent mixture for heteropoly acid formation; the second addition is the alkaline solution of luminol. In analogy with this, another set could be used for phosphorus(V) and silicon(IV). The coupling of the CL detection system with IC operation should be particularly attractive for on-site monitoring applications. The present IC–CL method was successfully applied to the determination of oxoanions such as arsenate, phosphate and silicate ions in a biological reference material (CRM 9 Sargasso), rice wine and water samples.

EXPERIMENTAL

Reagents and solutions

Eluent

According to the literature,[10] an eluent containing 0.015 M potassium nitrate and 0.01 M aqueous ammonia could be used. Potassium nitrate (reagent grade) and ammonia (guaranteed reagent for trace analysis) were purchased from Kanto Chemical (Tokyo, Japan) and Katayama Chemical Industries (Osaka, Japan), respectively. The eluent was prepared by dissolving potassium nitrate in water, adding ammonia (28% w/v) and diluting with water. HPLC-grade distilled water (Kanto Chemical) was utilized for eluent preparation.

Mixed reagent solutions for heteropoly acid formation

The following two reagent mixtures were prepared by dissolving ammonium metavanadate (reagent grade, Katayama Chemical Industries) in water, adding ammonium molybdate (reagent grade, Hayashi Pure Chemical Industries, Osaka, Japan) and sulphuric acid (analytical-reagent grade, Kanto Chemical), and diluting with water. One reagent consisted of 7.0 mM ammonium molybdate, 0.50 mM ammonium metavanadate

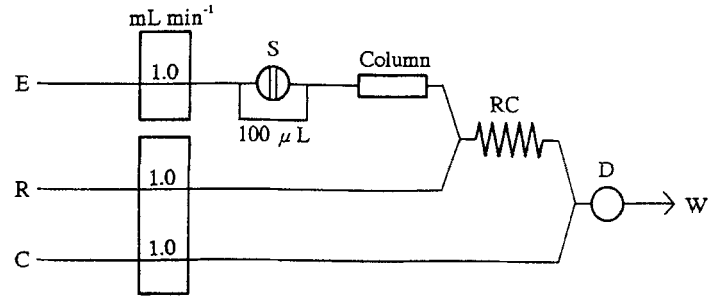

Figure 1 Flow system for IC separation and CL detection. E, eluent; R, reagent for heteropoly acid formation; C, reagent for the CL reaction; S, sample; RC, reaction coil; D, detector; W, waste.

and 20 mM sulphuric acid, and was used for determining arsenic(V), germanium(IV) and phosphorus(V). The other reagent used for the determination of silicon(IV) was a solution containing 23 mM ammonium molybdate, 0.50 mM metavanadate and 3.2 mM sulphuric acid.

Luminescent reagent solutions

The reagent solution of 3.0 mM luminol in 0.20 M sodium hydroxide which was used to determine arsenic(V), germanium(IV) and phosphorus(V) was prepared daily by dissolving luminol (general-purpose reagent, Aldrich Chemical, WI) in 4 M sodium hydroxide (analytical-reagent grade, Kanto Chemical) and diluting with water, while another solution of 0.60 mM luminol in 0.15M sodium hydroxide, used as a luminescent reagent for determining silicon(IV), was prepared daily in the same manner. The resulting solutions were allowed to stand for *ca.* 3 h before use, which gave reproducible CL signals.

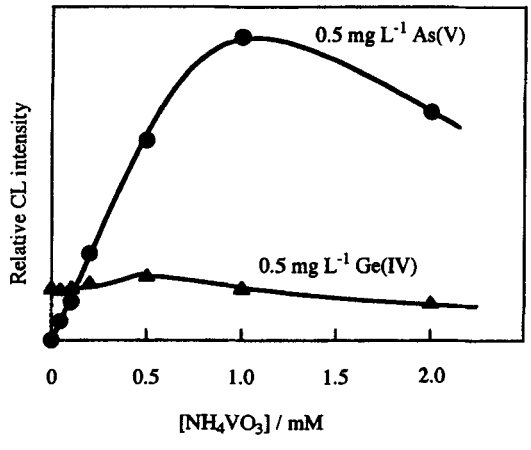

Figure 2 Variation of CL intensity with the metavanadate concentration for arsenic(V) and germanium(IV). Reagent mixture: ammonium molybdate, 7.0 mM; sulphuric acid, 20 mM; luminol, 0.6 mM; sodium hydroxide, 0.20 M.

Standard solutions

Commercially available 1000 mg l^{-1} atomic absorption standards of germanium(IV) (Hayasi Pure Chemical Industries), phosphorus(V) (Kanto Chemical) and silicon(IV) (Kanto Chemical) were used as stock standard solutions, respectively, whereas a 1000 mg l^{-1} stock standard of arsenic(V) was prepared by dissolving sodium arsenate (reagent grade, Kanto Chemical) in water. Working standard solutions were prepared by serial dilution of the respective stock standard solutions with water before use.

Deionized water

High-quality deionized water was obtained freshly from an Advantec Toyo (Tokyo, Japan) Model GSU-901 water purification system and was used for the preparation of all solutions, except for eluent. Plastic laboratory ware was used for solution preparation to avoid silicate contamination.

Sample solutions

A biological reference material, CRM 9 Sargasso, was supplied by the National Institute for Environmental Studies (NIES), Environmental Agency of Japan. A known amount of the powdered CRM 9 was weighed and digested according to the reported procedure[24] using a double-vessel method. Rice wine samples were used after appropriate dilution with water or as supplied. River water samples were filtered through a filter paper of 0.45 μm pore size.

Instrumentation and procedures

The flow system shown schematically in Fig. 1 was used for IC separation and CL detection. For

ion chromatography, a Tosoh (Tokyo, Japan) Model HLC-803D pump unit equipped with a rotary injection valve was used to drive the eluent stream at a constant flow rate of 1.0 ml min^{-1}. Samples were introduced into the stream using the injection valve with a 100 μl sample loop. A low-capacity IonPac AS4 anion-exchange column (250 mm × 4.0 mm i.d.; Nippon Dionex, Osaka, Japan) was employed for the chromatographic separation. The respective reagent solutions for heteropoly acid formation and luminol CL reactions were pumped separately at 1.0 ml min^{-1} via a Tosoh Model CCPM autocontrolled pump unit. All connections were achieved using PTFE tubing (0.5 mm i.d.).

The eluent was merged with the mixed reagent solution for heteropoly acid formation by means of a T-piece. The resulting solution was passed into a reaction coil (10 m × 0.5 mm i.d.) so that the formation of a heteropoly acid proceeded. The reaction coil was constructed of PTFE and wrapped in an ordinary band-type heater, maintained at 80 °C. After heating, the resulting solution was mixed with the luminol reagent in a 70 μl spiral flow cell housed in front of the photomultiplier tube of a Niti-on (Funahashi, Japan) Model LF-800 biochemiluminescence monitor; the CL signals produced were recorded on a strip-chart recorder.

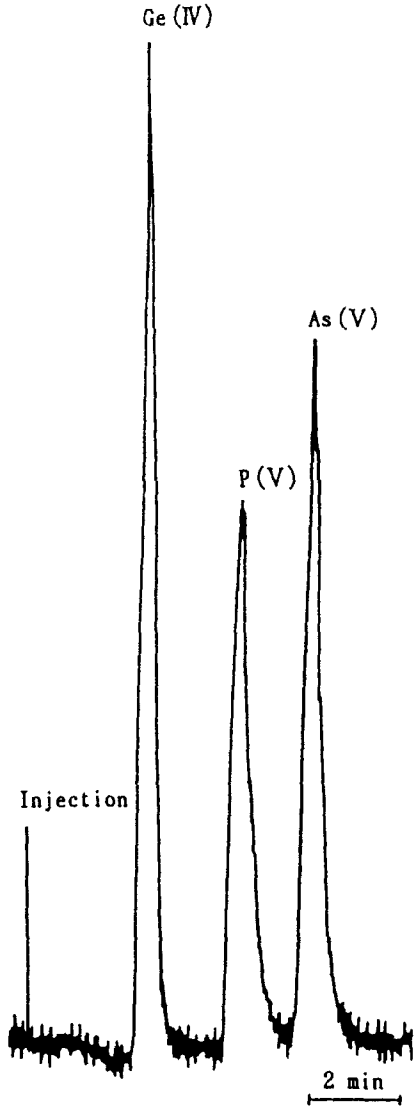

Figure 3 Chromatogram for a synthetic mixture (100 μl) of As(V) (0.5 mg l^{-1}), Ge(IV) (5 mg l^{-1}) and P(V) (0.05 mg l^{-1}) obtained with a 250 mm × 4.0 mm i.d. cation-exchange column and an eluent of NH_3 (0.01 M) and KNO_3 (0.015 M). Reagent mixture: ammonium molybdate, 7.0 mM; ammonium metavanadate, 0.50 mM; sulphuric acid, 20 mM; luminol, 3.0 mM; sodium hydroxide, 0.20 M.

RESULTS AND DISCUSSION

Luminol chemiluminescence with heteropoly acids

Even when molybdophosphoric acid was mixed with the luminol solution, some CL emission resulted but this was suppressed by excess molybdate ion. On the other hand, remarkable CL enhancement was achieved by addition of metavanadate to the reagent mixture. This implies that vanadium(V), as the heteropoly acid complexes[25] with phosphorus(V) and molybdate ($[PV_2Mo_{10}O_{40}]^{6-}$ and $[PVMo_{11}O_{40}]^{4-}$), might play an important role in the CL oxidation of luminol, although it has been pointed out that in reduction to Heteropoly Blues the role of the heteroatoms is in general insignificant.[26]

In early work on batch CL measurements based on the heteropoly acid reaction with luminol, ammonium metavanadate was added to the reagent mixture of ammonium molybdate and sulphuric acid in order to form the best heteropoly species for the respective CL determinations of arsenic(V),[20] germanium(IV)[21] and phosphorus(V),[22] whereas silicon(IV) was determined analogously without addition of metavanadate ion.[22] As shown in Fig. 2, the present flow CL results reveal that for CL

Table 1. Detection limits and dynamic ranges for arsenic(V), germanium(IV), phosphorus(V) and silicon(IV)

	Detection limit ($\mu g\ l^{-1}$)			Dynamic range
Analyte	Proposed IC–CL	Batch CL	IC–Abs[a]	($\mu g\ l^{-1}$)
As(V)	10	6[b]	100[e]	10[g]–1000
Ge(IV)	50	10[c]	400[e]	50[g]–25000
P(V)	1	4[d]	60[e]	1[g]–1000
Si(IV)	10	14[d]	30[f]	50[g]–10000

[a]Absorption spectrometry. [b]Data from Ref. 20. [c]Data from Ref. 21. [d]Data from Ref. 22. [e]Molybdenum Blue method (using 840 nm): data from Ref. 10. [f]Molybdenum Blue method (using 810 nm): data from Ref. 8. [g]Determination limit.

detection, ammonium metavanadate needs to be added to the reagent mixture for heteropoly acid formation with arsenic(V). Increasing metavanadate concentration in the reagent mixture caused an increase in the CL emission; maximum emission occurred at around 1.0 mM metavanadate. Such an increase in CL by metavanadate addition also occurred with phosphorus(V). For germanium(IV) (Fig. 2) and silicon(IV), on the other hand, when the reagent mixture was run in the absence of metavanadate, CL emission was obtained and the metavanadate concentration had only a slight influence on the CL intensity. However, further work will be needed to elucidate the role of metavanadate and the difference between the effects of its concentration on the CL emission with arsenic(V) and germanium(IV) (Fig. 2).

Optimization studies

A recent study on the use of Molybdenum Blue as a post-column detection system for the determination of arsenic(V), germanium(IV), phosphorus(V) and silicon(IV) revealed that it was difficult to find a single set of reagent conditions to give good sensitivity for all four analytes.[10] Also, optimum reagent conditions reported for the batch CL procedure using the reaction of heteropoly acids with luminol varied with the analytes.[20–23] Further optimization studies of the reagent conditions would therefore be

Table 2. Determination of arsenic(V), phosphorus(V) and silicon(IV) in various samples

		Concentration ($mg\ l^{-1}$)			
		Method			
Sample	Analyte	Proposed	Other	Certified value	Reference value
Sargasso[a]					
	As(V)[b]	0.447, 0.473		0.452±0.002	
	P(V)[c]	0.512, 0.508			0.512
River water					
A	P(V)	0.277, 0.286	0.280[d]		
	Si(IV)	18.8, 19.5	17[e]		
B	P(V)	0.265, 0.261	0.240[d]		
	Si(IV)	19.8, 20.8	19[e]		
Rice wine					
A	P(V)	43.5, 43.5	45.6[f]		
B	P(V)	61.5, 57.5	60.4[f]		

[a]NIES CRM 9. [b]Sample taken: 0.394 g in 100 ml. [c]Sample taken: 0.0197 g in 100 ml. [d]CD. [e]AA. [f]ICP–AE.

needed to develop a sensitive post-column detection system based on the luminol reaction for CL determination after IC separation. In this work, using the aforementioned flow system, an attempt was made to ascertain the suitability of the chemistry of the heteropoly acids as the post-column reactants. Each of the sulphuric acid, ammonium molybdate, ammonium metavanadate, luminol and sodium hydroxide concentrations given in the literature[20–23] was modified individually, and the corresponding effects on the CL signals were observed.

Recently, good analytical separations using a mobile phase of aqueous ammonia (0.01 M) and potassium nitrate (0.015 M) with a Dionex HPLC-AS4 column were reported for mixtures of arsenic(V), germanium(IV) and phosphorus(V) or arsenic(V), phosphorus(V) and silicon(IV).[10] In this work, the same eluent conditions were used, since the mobile phase has only a slight influence on the luminol CL reaction. However, this eluent may affect heteropoly acid formation which progresses in an acidic medium. In addition, incompatibility of heteropoly acid formation and the subsequent CL reaction conditions was considered to be another problem, because of the alkaline solutions used for the latter. These problems were resolved by careful choice of the reagent concentrations.

One reagent mixture of ammonium molybdate (7.0 mM), ammonium metavanadate (0.50 mM) and sulphuric acid (20 mM) for heteropoly acid formation was found to be suitable for determining arsenic(V), germanium(IV) and phosphorus(V) based on the CL reaction of heteropoly acids with a solution of 3.0 mM luminol and 0.20 M sodium hydroxide. To optimize the CL sensitivity for arsenic(V) only, further modifications were made to the metavanadate and luminol concentrations; a metavanadate concentration of 1.0 mM and a luminol concentration of 0.6 mM were recommended. However, these reagent mixtures were completely unsuitable for CL determination of silicon(IV). As has been pointed out, generally the silicon(IV) determination was conducted at lower acid levels than for arsenic(V) and phosphorus(V),[1,10] and so the reagent mixture was modified by decreasing the acid concentration and increasing the molybdate concentration to be optimized for the maximum response of silicon(IV). Consequently, another reagent mixture of ammonium molybdate (23 mM), ammonium metavanadate (0.50 mM) and sulphuric acid (3.2 mM) was indicated as suitable for the CL determination of silicon(IV) with a luminescence reagent of 0.60 mM luminol in 0.15 M sodium hydroxide. For phosphorus(V), this set of reagent conditions gave as good a sensitivity as the above set but it gave poor sensitivity for arsenic(V) and germanium(IV). Although a chromatographic separation for a mixture of germanium(IV) and silicon(IV) under the eluent conditions used here was not possible,[10] the results suggest that these species could be detected separately by using the respective sets of reagent conditions for the mixture.

As mentioned above, heteropoly acid formation was kinetically slow for the oxoanions.[22] This was confirmed by the fact that larger CL responses were achieved when the reaction coil volume was increased. Furthermore, as the temperature was elevated, so the sensitivity improved. In those cases, however, broadening of the CL signals was caused, resulting in poorly resolved peaks. To obtain an analytically useful peak shape with a reasonable analysis time, a 10 m × 0.5 mm i.d. reaction coil was chosen as optimal, and the reaction temperature was kept at 80 °C.

Figure 3 shows a typical chromatogram resulting from the injection of a synthetic mixture of 0.5 mg l^{-1} arsenic(V), 5 mg l^{-1} germanium(IV) and 0.05 mg l^{-1} phosphorus(V). The three species were completely resolved from each other.

Sensitivity and dynamic range

An increase in the background CL signal was considered as the analytical CL signal and a detection limit (DL) was defined as the concentration of the analyte for which the analytical signal is three times greater than the noise level of the baseline. DLs for arsenic(V), germanium(IV), phosphorus(V) and silicon(IV) were obtained by injection of a 100 μl sample in the present IC–CL system, under the optimized conditions, and are listed in Table 1. The DL values are superior to those attained by IC using a Molybdenum Blue post-column detection system,[6–10] and compare favourably with those obtained by batch CL measurements[20–23] (Table 1). In this work, incorporating the advantages of FI into the sensitive CL method provided a rapid and reproducible method for the determination of the four analytes. Linear calibrations were obtained for the analytes and the linear dynamic

ranges are also listed in Table 1. The relative standard deviations found using five replicate injections of a mixed standard containing arsenic(V) (0.5 mg l^{-1}), germanium(IV) (5 mg l^{-1}) and phosphorus(V) (0.05 mg l^{-1}), and of a standard of silicon(IV) (0.5 mg l^{-1}), were 2.1, 0.6, 3.7 and 1.6%, respectively.

Analytical applications

To evaluate the quantitative performance and accuracy of the proposed IC–CL method, arsenic(V) and phosphorus(V) in a biological reference material, Sargasso (NIES CRM 9), phosphorus(V) and silicon(IV) in river water, and phosphorus(V) in rice wine, were determined. The calibration graphs obtained under the optimum conditions were used directly for the determinations and the results are given in Table 2. The data for arsenic(V) and phosphorus(V) in the biological sample are in good agreement with the certified and reference values, respectively. To verify the results for phosphorus(V) and silicon(IV), furthermore, measurements by a conductivity detection method (CD), flame atomic absorption spectrometry (AA) or inductively coupled plasma atomic emission spectrometry (ICP–AE) were performed for the river water and rice wine samples. These data are consistent with the corresponding data obtained by the present IC–CL method.

The analytical results indicated that the CL system is suitable as a sensitive detector for IC and that potential CL interferences from metal ions in the samples could be eliminated sufficiently by IC. Thus, the proposed IC–CL method is valid and would be applicable to the determination of arsenate, germanate, phosphate and silicate ions in biological and environmental samples. However, before this method can be applied to samples of a biological and environmental nature, analytical efforts are certainly needed to identify further potential interferents.

Further investigations into the use of this method for the analyses of other oxoanions are now in progress.

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