Short communication

# Fluorimetric determination of magnesium and aluminum via complexation with oxine in high-performance liquid chromatography

Toyohide Takeuchi*, Shiro Inoue, Mamie Yamamoto, Miharu Tsuji, Tomoo Miwa

*Department of Chemistry, Faculty of Engineering, Gifu University, 1-1 Yanagido, Gifu 501-1193, Japan*

## Abstract

Aluminum and magnesium were determined by fluorimetric detection via pre-column and/or in-column derivatization with 8-hydroxyquinoline (oxine) in high-performance liquid chromatography. The oxine complex of aluminum was selectively detected when the eluent contained no oxine, whereas the aluminum and magnesium complexes could be simultaneously detected when the eluent contained oxine. The sensitivity was improved by using eluents containing oxine by a factor of 7.1 for aluminum, and the detection limits at $S/N=3$ were 18 and 16 ng/ml for magnesium and aluminum, respectively. The present system was applied to the determination of magnesium and aluminum in various water samples. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Derivatization, LC; Magnesium; Aluminum; Oxine

## 1. Introduction

Derivatization with 8-hydroxyquinoline (oxine) followed by liquid–liquid extraction is a well-known method for the determination of metal ions [1]. Liquid chromatography (LC) has been used for the determination via complexation complexes of various metals with oxine as well as with its 5-sulfonic acid derivative [2–12]. Derivatization of metals with oxine has been carried out by pre-column or in-column methods. In-column derivatization of metal ions to oxinates has been attempted in reversed-phase LC, where oxine is added to the solvent and the metal oxinates are formed during the chromato-graphic process, followed by UV–Vis detection [2,3]. Hoffmann and Schwedt [3] concluded that in-column derivatization is fast and easy because the samples can be injected directly onto the column, and it gives better results than pre-column derivatization.

A fluorimetric method with oxine in the kinetic-differentiation mode was developed to determine aluminum in micellar liquid chromatography [4,5]. Oxine forms complexes with a number of metals, but only a few of them are fluorescent. The method [4] is based on the fact that oxine complexes with metals formed are not very stable. In other words, oxine complexes easily undergo solvolytic reaction during chromatography. Since the aluminum and cobalt complexes are relatively stable, they can be detected even if the eluent contains no oxine, whereas other

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*Corresponding author. Tel./fax: +81-582-932-806.
*E-mail address:* takeuchi@apchem.gifu-u.ac.jp (T. Takeuchi).

metal complexes decompose in the column prior to detection or are transparent to fluorimetric detection [5]. That is, the method provides a selectivity with some sacrifice of sensitivity. However, since oxine complexes are not stable, the signal intensity is likely to depend on the operating conditions, leading to poor repeatability.

This paper examines eluent conditions for the fluorimetric determination of aluminum via complexation with oxine in reversed-phase LC. The use of eluents containing oxine is proposed to improve the sensitivity for aluminum, and it turns out that magnesium can also be determined in various water samples without any interference. The present system is applied to the simultaneous determination of magnesium and aluminum in various water samples.

## 2. Experimental

### 2.1. Apparatus

The LC system comprised a 880-PU high-performance liquid chromatography (HPLC) pump (Jasco, Tokyo, Japan), a Model FP-920 fluorimetric detector (Jasco), a Model 9725 valve injector with a 20-μl loop (Rheodyne, Cotati, CA, USA), an L-column ODS column (150×4.6 mm I.D.; Chemicals Evaluation and Research Institute, Tokyo, Japan), and a Chromatopac C-R7Ae plus data processor (Shimadzu, Kyoto, Japan).

### 2.2. Reagents

The reagents employed were of reagent grade and obtained from Nacalai Tesque (Kyoto, Japan), unless otherwise noted. Acetonitrile was of HPLC grade, and purified water was prepared by a Milli-Q Plus system (Millipore, Molsheim, France). *N,N*-Bis(2-hydroxyethyl)-2-amino-ethanesulfonic acid (BES) was obtained from Wako (Osaka, Japan).

### 2.3. Derivatization with oxine

Samples were derivatized before injection unless otherwise noted. Derivatization of samples was carried out by mixing the following solutions in this order at room temperature: 0.5 ml of sample solu-

tion, 0.5 ml of 12 m*M* oxine in 20% acetonitrile, 0.5 ml of 2.5 *M* BES (pH 7.0) in 20% acetonitrile and 0.5 ml of 0.32 *M* SDS. After mixing the solution, a 20-μl volume of sample solution was loaded by the loop injector. As for in-column derivatization, 0.5 ml of purified water was added instead of the oxine solution in the above preparation.

## 3. Results and discussion

### 3.1. Effect of oxine concentration in the eluent for pre-column derivatization

When the eluent contains a chelating agent, the samples can be injected directly onto the column, and it gives better results compared to pre-column derivatization. However, since the addition of oxine or its 5-sulfonic acid derivative leads to the increase in the background of UV–Vis detectors employed, the concentration of the chelating agent in the mobile phase can not be easily optimized [6,7,10]. Bailocchi et al. [6] reported that aluminum(III) could not be detected owing to its high lability, where 0.1 m*M* 8-hydroxyquinoline-5-sulfonic acid (HQS) is contained in the eluent. Shijo et al. [7] also used an eluent containing HQS, but they suffered from higher noise due to HQS and selected 0.1 m*M* HQS as the optimum. Fluorimetric detection solves the above noise problems because oxine or HQS is not fluorescent. Fluorimetric detection also makes optimization of the chelating agent concentration much easier, leading to sensitive detection of aluminum.

In the case of pre-column derivatization, magnesium and aluminum can be detected when the eluent contains oxine. On the contrary, aluminum alone can be detected when the eluent contains no oxine. Fig. 1 shows the effect of the oxine concentration on the peak height. It is seen that the peak height increases with increasing oxine concentration for magnesium and aluminum to an oxine concentration up to 25 m*M*. The eluents employed in the figures are 30% acetonitrile aqueous solutions in 80 m*M* sodium dodecyl sulfate (SDS) and 50 m*M* sodium phosphate buffer (pH 7.0) containing 0 to 25 m*M* oxine, where SDS is added to enhance the fluorescence intensity owing to the micelle effect [5].
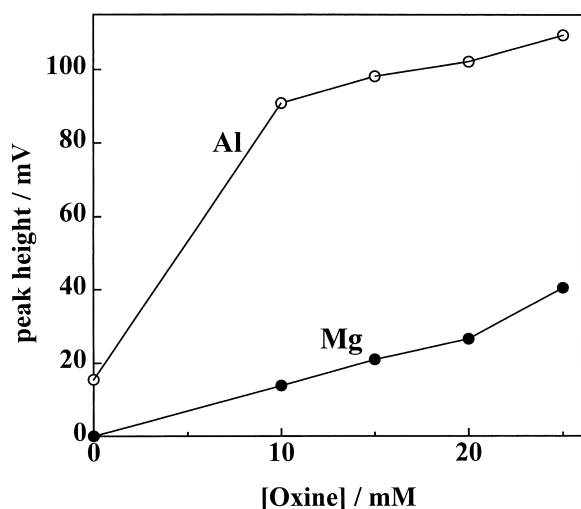
Fig. 1. Effect of oxine concentration on the peak height. Column: 150×4.6 mm L-column ODS. Eluent: 30% acetonitrile aqueous solutions in 80 m$M$ SDS and 50 m$M$ sodium phosphate buffer (pH 7.0) containing oxine. Flow-rate: 1.0 ml/min. Wavelengths of detection: excitation at 370 nm and emission at 516 nm. Injection volume: 20 μl. Analytes: 1 m$M$ magnesium (pre-column derivatized) and 0.1 m$M$ aluminum (pre-column derivatized).

The analyte loaded is 1 m$M$ magnesium or 0.1 m$M$ aluminum derivatized with oxine before injection, i.e., pre-column derivatization. As for aluminum, the peak was slightly fronting when the oxine concentration in the eluent was 10–20 m$M$. The smaller the oxine concentration, the more severe the fronting observed. This may be because a portion of aluminum trioxinate, which elutes in around 6 min under the conditions in Fig. 1, loses oxinate ligands at lower oxine concentrations and forms dioxinate or monooxinate complexes of aluminum. The peak height of aluminum for 25 m$M$ oxine was increased by a factor of 7.1, compared to that observed without oxine. It should be noted that magnesium could not be detected when the eluent contained no oxine.

On the other hand, the retention times of the oxine complexes of magnesium and aluminum were nearly constant, independent of the oxine concentration. Although the solubility of oxine in the eluent employed in Fig. 1 is ca. 100 m$M$, 25 m$M$ oxine was employed for the following experiments considering the stability of the separation column.

### 3.2. In-column derivatization

When eluents contained oxine, magnesium and aluminum could be detected even if derivatization of the sample solution was not carried out before injection. In this case, oxine complexes of magnesium and aluminum complexes were formed in a column during chromatographic processes (in-column derivatization). However, the aluminum peak was skewed for the in-column derivatization because of coexistence of multiple components in equilibrium. Fig. 2 compares the chromatograms obtained under different conditions. Fig. 2A and B were obtained by using eluents containing oxine at 25 m$M$, whereas Fig. 2C was obtained by using an eluent containing no oxine. Underivatized analytes are injected in Fig. 2B, whereas derivatized analytes are injected in Fig. 2A and C. It is seen that Fig. 2A achieves higher signals and gives more symmetric peaks than Fig. 2B and C. The conditions in Fig. 2C correspond to those of the kinetic-differentiation mode [4,5]. It can be concluded that in terms of sensitivity eluents should include oxine and analytes should be derivatized prior to injection.
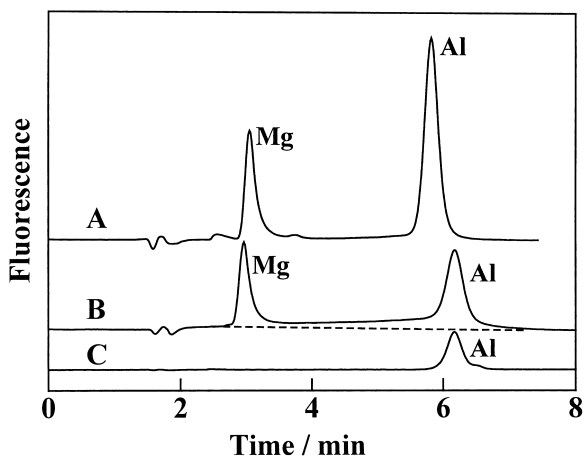


Fig. 2. Separation of magnesium and aluminum under different conditions. Eluent: 30% acetonitrile aqueous solutions in 80 m$M$ SDS and 50 m$M$ sodium phosphate buffer (pH 7.0) containing oxine at 25 m$M$ (A and B) or 0 m$M$ (C). Analytes: 0.2 m$M$ magnesium and 0.02 m$M$ aluminum. Analyte derivatization: pre-column derivatized for A and C; in-column derivatized for B. Other operating conditions as in Fig. 1.

Post-column reaction followed by fluorimetric detection is another option for the determination of aluminum. Kokot and Pawlacyzyk [12] separated aluminum in cation-exchange chromatography and visualized it by following post-column reaction with HQS. They found that interference from magnesium was severe and sample solutions had to be diluted. Since the present system contains higher concentration of oxine, the interference from magnesium was not observed. The present system employs a single pump, which provides a much simpler LC system compared to the post-column reaction system.

### 3.3. Analytical figures of merit

Under the conditions in Fig. 2A, the peak height was linear to the analyte concentration up to 1.0 and 0.1 m$M$ for magnesium and aluminum, respectively. When the concentrations of magnesium and aluminum were 1.0 and 0.1 m$M$, respectively, the relative standard deviations of the retention time, peak area and peak height of magnesium for five successive measurements were 0.16, 1.0 and 2.1%, respectively, whereas those for aluminum were 0.08, 1.4 and 1.2%, respectively.

The detection limits at $S/N=3$ under the conditions in Fig. 2A were 0.74 $\mu M$, 18 ng/ml or 0.36 ng for magnesium. On the contrary, the blank of aluminum, which was attributed to water, acetonitrile and the other reagents, was significant, e.g., 0.60 $\mu M$, 16 ng/ml or 0.32 ng of injection. It is inevitable to lower the blank in order to achieve lower detection limits for aluminum.

Zinc and calcium, which are commonly contained in water samples, gave no signal under the conditions in Fig. 2A.

### 3.4. Application to water samples

The present detection system could be applied to the determination of magnesium and aluminum contained in various water samples such as river water, rainwater and tap water. The concentrations of magnesium were determined to be 0.68, 0.034 and 0.22 $\mu$g/ml for river water, rainwater and tap water, respectively. On the contrary, the concentrations of aluminum were determined to be 70, 84 and 92 ng/ml for river water, rainwater and tap water, respectively.

## 4. Conclusion

Magnesium and aluminum contained in water samples could be selectively determined by using eluents containing oxine. The pre-column derivatization with eluents containing oxine improved the sensitivity of aluminum by a factor of 7.1, compared to the data achieved by the kinetic-differentiation mode [4,5]. The present system allows selective and sensitive simultaneous determination of magnesium and aluminum.

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