ACTA CHROMATOGRAPHICA, NO. 14, 2004

MICELLAR LIQUID CHROMATOGRAPHIC DETERMINATION OF ALUMINUM AS ITS COMPLEX WITH 8-HYDROXYQUINOLINE-5-SULFONIC ACID

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SUMMARY

A micellar liquid-chromatographic method is proposed for determination of Al(III) as the 8-hydroxyquinoline-5-sulfonic acid derivative, with spectrofluorimetric detection. Cetyltrimethylammonium bromide, a cationic surfactant (0.05 M), was used as mobile phase. The metal chelate was detected at λ_{Ex} 410 and λ_{Em} 510 nm. Response to aluminum is selective in the presence of other metal ions. The method eliminates the need for addition of reagent or organic modifier to the mobile phase, as is normal in RP HPLC. Under optimized conditions the linear range was 20–200 μg L^{-1} Al(III), the limit of detection 10 μg L^{-1}, and the limit of quantification 40 μg L^{-1}. The method was used to determine aluminum in a variety of water samples.

INTRODUCTION

Studies of secondary equilibria (acid–base, complexation, formation of ion-pairs, and solubilization) in reversed-phase high-performance liquid chromatography (RP HPLC) have gained momentum in recent years. The use of surfactant solutions at concentrations above the critical micelle concentration (cmc) as mobile phases in reversed-phase HPLC has given birth to micellar liquid chromatography (MLC) which, although in its initial stages of development, has the potential to replace RP HPLC with aqueous –organic mobile phases [1]. Sensitivity of determination is increased, because for many substances the intensity of luminescence, low temperature phosphorescence, and absorption are enhanced in the presence of surfactants.

The ecological and biological significance of aluminum has been an important subject in the last two decades. The presence of this element

in drinking water is of major concern as a potential threat to the health of several species including humans. Aluminum salts, for example alum, are, unfortunately, often used as a flocculating agent in the treatment of drinking water and aluminum pots are used daily to boil drinking water and to cook food, especially in developing countries, for example Pakistan [2].

A variety of methods for determination of aluminum have been reported in the literature, e.g. liquid chromatography [2], spectrophotometry [3], fluorimetry [4], and atomic spectroscopy [5]. At low levels graphite furnace atomic absorption spectroscopy is used; this is, however, expensive and not feasible for routine analysis. 8-Hydroxyquinoline (8-HQ) has been used as pre-column derivatizing reagent in the determination of a variety of metal ions by RP HPLC [6]. Aluminum reacts with three molecules of this reagent (Fig. 1) to give an ion associate complex which can be extracted into an organic solvent. Because the complex has absorption and fluorescent properties it can be used for determination of aluminum spectrophotometrically or fluorimetrically. Lability of 8-hydroxyquinoline complexes in HPLC under hydrodynamic conditions has been reported and most workers have added 8-HQ to the mobile phase to ensure the stability of the complex. This introduces background absorption or florescence, which reduces sensitivity. Yotsuyanagi et al. reported the determination of aluminum with 8-quinonolinol, by kinetic differentiation mode micellar liquid chromatography, with a solution of TX-100 (a non-ionic surfactant) in acetonitrile as mobile phase [2,7].

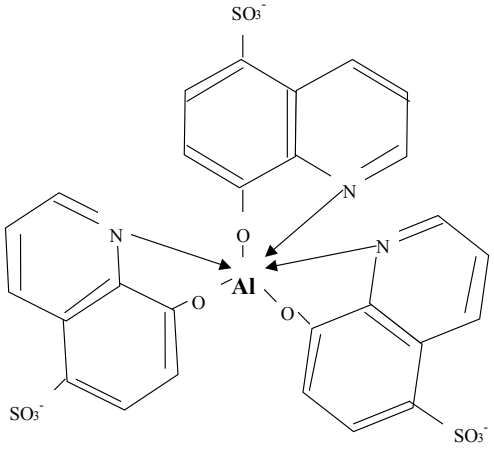

Fig. 1

Structure of the Al-HQS complex

In this work cetyltrimethylammonium bromide (CTAB) has been used as micellar mobile phase and hydroxyquinoline-5-sulfonic acid as chelating agent; this overcomes difficulties reported previously [8] and provides enhanced sensitivity, selectivity, and increases the life of the chromatographic column.

Non-ionic, cationic, and anionic surfactants enhance luminescence, depending on the nature of the surfactant and the species being analyzed [9]. The fluorescence of negatively charged complexes of hydroxyquinoline sulfonic acid is enhanced by cationic surfactants. Such surfactants have several advantages, including solubilization of the Al-HQS complex, enhancement of fluorescence intensity, and elimination of the need for reagent in the mobile phase. The fluorescence enhancement is a result of strong ionic interactions between the positively charged surfactants and the negatively charged complex. It has been reported that when electrostatic and hydrophobic effects occur concurrently at the micellar level maximum enhancement of fluorescence intensity was achieved as a result of the formation of a more rigid structure [10].

EXPERIMENTAL

Sample Preparation

Appropriate volumes of sample (50–200 μL) were placed in a 2.0-mL flask and 100 μL 1% ascorbic acid was added to reduce Fe(III) and Cu(II). The pH was adjusted to 5.5 with NaOH (0.1 M) and 0.5 mL 1% hydroxyquinoline and 0.5 mL 0.3 M surfactant (to solubilize the complex formed) were added and the pH was adjusted to 8.5 with 0.1 M NaOH (20 μL 0.1 M NaOH is sufficient to increase the pH to 8.5). The mixture was then diluted to volume with water and the solution obtained (10 μL) was analyzed by HPLC.

Procedure

Chromatography was performed with an Hitachi LC-Organizer HPLC system with L-6200 pump and Rheodyne injection port. Samples were separated on 25 cm × 4.6 mm i.d. SGE LiChrosorb ODS column (particle size 5 μm, pore size 80 Å). The mobile phase was 0.05 M CTAB at pH 8.0 and the flow rate 1 mL min^{-1}. Detection was performed with a F-1050 fluorescence spectrophotometer with 410 and 510 nm as the excitation and emission wavelengths. A PC running CSW32 software was used

for integration and calculation. Before HPLC analysis the column was equilibrated thoroughly with 0.05 M CTAB as mobile phase.

A Shimadzu RF-510 spectrofluorimeter was used to scan the excitation and emission spectra of complexes of different metal ions with HQS.

Results obtained by use of a Perkin–Elmer Optima 2000DV ICP optical emission spectrometer were compared with results obtained by the proposed method.

RESULTS AND DISCUSSION

Selection of the Surfactant

Different surfactants, for example Brij-35 (non-ionic), SDS (anionic), and CTAB (cationic) were investigated as mobile phases. Although non-ionic and anionic surfactants result in adequate solubility of the complex, because a reagent to stabilize the hydrodynamically unstable complex of aluminum is also required in the mobile phase, the cationic surfactant cetyltrimethylammonium bromide (CTAB) was selected as the surfactant of choice.

Effect of pH on Precolumn Derivatization

It was found that the samples analyzed must be within the pH range 5.0–6.0, because below this pH Fe and Cu react and nearly no reaction occurs with aluminum. Because pH also affects fluorescence after complex formation, complexation was performed at pH 6.0 and the pH was then

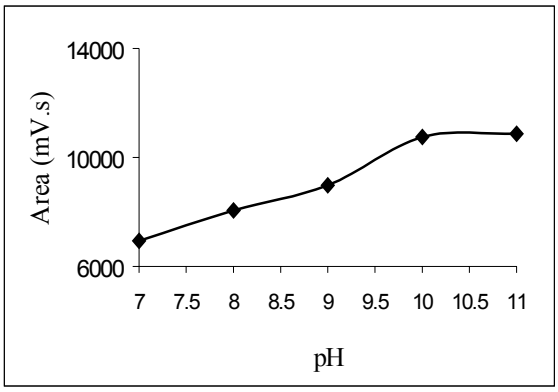

Fig. 2

Effect of pH on the size of the chromatographic peak obtained for 100 ppb aluminum

varied, by addition of 0.1 M NaOH, to find the value which resulted in the optimum fluorescence intensity. Figure 2 shows the effect of pH on florescence intensity; pH 8.5 was taken as optimum for pre-column derivatization and mobile phase was adjusted to pH 8.0.

Effect of HQS Concentration

The concentration of HQS was varied by adding different volumes of 1% HQS. Figure 3 shows the effect of HQS on fluorescence intensity (peak area). For a 100 ppb solution of aluminum 30 µL 1% HQS was sufficient but when other ions, for example Fe, Cu, and Mg were present, more HQS was required. Hence 500 µL HQS was used in subsequent work.

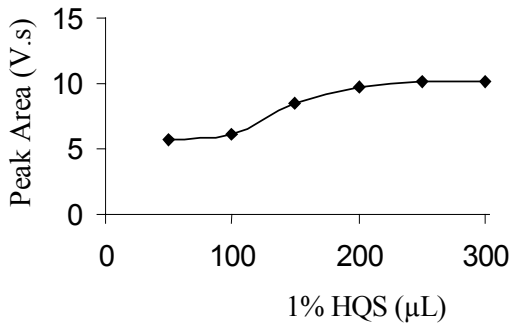

Fig. 3

Effect of reagent concentration on the size of the chromatographic peak obtained for 100 ppb aluminum

Effect of Surfactant Concentration

Figure 4 shows the effect of CTAB concentrations between 0.02 and 0.1 M on the intensity of the peak of the aluminum complex. It was found that 0.05 M CTAB was enough to solubilize and elute Al-HQS from the HPLC column. Concentrations above 0.1 M could not be used because column back-pressure exceeded normal operating conditions.

Spectral Characteristics

A variety of metal ions (Cd, Zn, Fe, Mn, Be, Al, Cu, In, Ga, and La) which react with hydroxyquinoline to give chloroform-extractable complexes [11] were investigated to determine their fluorescent behavior in CTAB

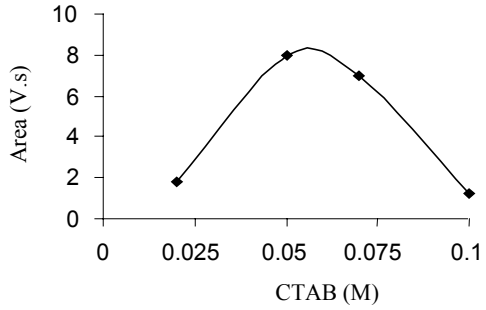

Fig. 4

Effect of surfactant concentration on the size of the chromatographic peak obtained for 100 ppb aluminum

micellar medium. Maximum fluorescence was obtained for aluminum; fluorescent intensity for cadmium and indium was 70% and 64%, respectively. λ_{ex} and λ_{em} for the aluminum complex were 410 and 510 nm. Although the absorption behavior for Fe, Mn, Zn, Cd, La, and Cu was good it was not reproducible under the chromatographic conditions used.

Interference

The metal cations that form absorptiometric complexes in the ammoniacal pH range were selected for interference and spectral study [11]. In the spectral study of metal complexes with 8-hydroxyquinoline-5-sulfonic acid fluorescence behavior was observed for aluminum, cadmium, and indium only. When complexes of these metals were analyzed by HPLC, a response was obtained for aluminum only. It has recently been reported by Takeuchi et al. [7] that magnesium and aluminum can be determined simultaneously by using hydroxyquinoline in the mobile phase. In our work the response to aluminum was more selective than that to all other metal ions under the chromatographic conditions used, because the other ions are labile to hydrophobic interactions.

Because copper and iron are naturally present in water systems and form absorptiometric complexes with HQS, solutions containing salts of copper and iron in different oxidation states were injected to observe the effect of these on the chromatographic signal. It was observed that in the presence of iron(III) and copper(II) the fluorescence intensity decreased appreciably whereas at low levels Fe(II) and Cu(I) do not interfere. Thus in the sample-preparation step the higher oxidation states of these metals were reduced to the lower oxidation states by use of ascorbic acid.

Iron(II) and copper(I) are potential absorptiometric interferences and thus reduce the availability of the reagents to aluminum. At higher reagent concentrations, however, tolerance limits for Fe(II) and Cu(I) are, respectively, 500 and 100 times higher than that of aluminum.

Analytical Figures of Merit

The calibration plot shows linearity over the range 20–200 ng mL^{-1}. The equation of the straight line is $y = 201.0641x + 75.82$ ($R = 0.998$). The limit of detection was 10 ng mL^{-1}, or 0.01 ng per injection (3σ), and the limit of quantification was 40 ng mL^{-1} or 0.04 ng per injection (10σ); the coefficients of variation were 2.6% and 1.9%, respectively.

Application

The concentration of aluminum in different surface water samples (running and stored) was examined by use of the procedure described above. The water samples were from a water supply storage tank located at the K.B. feeder of the river Indus at Jamshoro, Sindh, Pakistan, and tap water samples from a residential area located in the vicinity of Jamshoro. Results obtained by use of the proposed method and by use of ICP–AES are compared in Table I. The results were statistically validated by use of a two tailed *t*-test (paired two samples for mean). There was good agreement between results obtained by use of the two methods; the Pearson correlation coefficient was 0.998 and the *t* value 3.18, which is much less than the tabulated value (4.303) for $n = 3$ at 95% confidence level.

Table I

Determination of Al(III) in different water samples, as the HQS complex by MLC and by ICP–AES

Sample	ICP–AES (mg L^{-1})	Proposed method (mg L^{-1})
S1	1.11 ± 0.01	0.99 ± 0.03
S2	3.14 ± 0.01	3.04 ± 0.01
S3	0.710 ± 0.03	0.700 ± 0.04
S4	0.749 ± 0.02	0.610 ± 0.02

$n = 3$

CONCLUSION

Aluminum in water samples can be selectively determined by MLC. The method does not require use of a reagent in the mobile phase. Use of cationic surfactant and a negatively charged complex enhances the sensitivity and selectivity of the determination.

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