

Suction-Flow Injection/On-Line Preconcentration System with Oxine-Loaded Active-Carbon Column and Its Application to Sensitive Determination of Copper by Atomic Absorption Spectrometry

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ABSTRACT

Suction-flow injection/on-line column preconcentration of copper(II) from an aqueous solution for atomic absorption spectrometry (AAS) was investigated utilizing a column packed with gas chromatographic-grade porous active-carbon impregnated with 8-quinolinol. An aliquot of sample solution was sucked into a buffer solution line, mixed and pumped through the column, and segmentation was proceeded by compressed-air. Sequentially the analyte was eluted and directly introduced into the nebulizer of the AA spectrometer. Using 10 cm³ of the sample solution, this method gave a signal enhancement of one order of magnitude for copper, better than that obtained by a conventional nebulization system; the detection limit was 4.4 ng cm⁻³ with a sampling rate of 20 h⁻¹. The relative standard deviation for 300 ng cm⁻³ copper was 2.0% (n=5). The same column could be used for more than 60 replicate analyses. The proposed method was applied to the determination of copper in certified reference materials.

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INTRODUCTION

Several papers have been published recently on the possibility of on-line sample introduction system incorporated with ion-exchange preconcentration for atomic spectrometry in order to perform a determination of metal ions in trace amounts. In addition to other benefits of improving the detection limits and separating the analytes from interfering matrices, these systems have the advantage of being able to carry out operation in a closed system.¹⁻³

On the other hand, in batch procedures, despite the smaller exchange capacity and less hydrophilicity, active carbon has been used as a sorbent.⁴⁻⁶ In order to improve the collection capacity, several batch methods for the concentration of trace metals on chelating agent-loaded active carbon have been reported.⁷⁻¹³ However, these methods are somewhat tedious for a preconcentration procedure, and none of them makes replicate use of the active carbon. We reported a low-cost on-line preconcentration system using a column packed with porous active carbon of high purity impregnated with 8-quinolinol (oxine-AC) for the inductively coupled plasma atomic emission spectrometry of cadmium(II), where multiple use of oxine-AC was possible without any reloading with oxine.¹⁴ In this paper, we report the construction of a suction-flow injection/on-line introduction system for flame atomic absorption spectrometry (AAS), in which all the operations including sample loading, mixing with buffer solution, segmentation by air and elution with nitric acid can be carried out automatically. The purpose of this paper is to demonstrate the potential of the system together with its application to trace copper determination in NBS and NIES standard environmental and steel samples.

EXPERIMENTAL

Reagents

Water was purified by ion-exchange followed by filtration using an Advantec Toyo Model GSU-901 de-ionizer. Analytical-reagent grade chemicals were used in all experiments. A $1000 \mu\text{g cm}^{-3}$ copper(II) standard solution (Kanto Chemical) was used by appropriate dilution with dilute nitric acid. A citrate buffer solution (0.05 mol dm^{-3}) was prepared by dissolving 11.3 g of diammonium hydrogen citrate in 1.0 dm^3 ; the pH was adjusted to 3.0 with 1 mol dm^{-3} nitric acid. Gas chromatographic-grade active carbon (80-100 mesh, GL Sciences) was used. The preparation of the oxine-AC was prepared according to the literature.¹⁴

Apparatus

A Shimadzu Model AA-610S atomic absorption spectrometer equipped with a Hamamatsu Photonics copper hollow-cathode lamp, operated at 10 mA and at wavelength of 324.7 nm, was used under a recommended air-acetylene flame condition.

The design details of the oxine-AC column are shown in Fig. 1. The column was made of a 2-mm i.d. Teflon tube. The length of the AC layer was 10 cm and both ends of the column were packed with a small amount of quartz wool.

A prototype

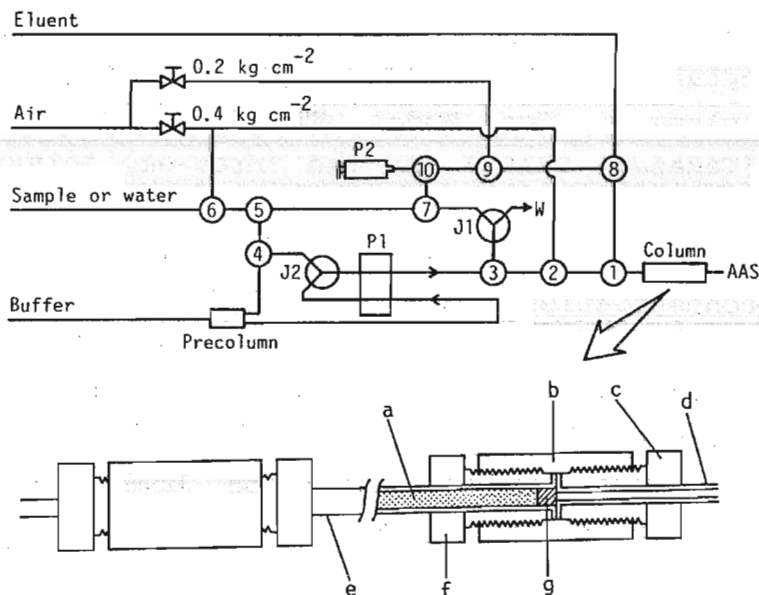


Fig. 1 Schematic diagram of manifold for the on-line column preconcentration system.

P1, peristaltic pump; P2, syringe pump; 1-10, three-way solenoid valves; J1-J2, three-way joint; W, waste; column, oxine-AC; precolumn, Muromac A-1; a, oxine-AC; b, Teflon coupling; c, flare-fit adapter; d, Teflon tube; e, quartz wool.

of Nippon Jarrell-Ash Model SC-100 suction flow column unit was used for the on-line preconcentration system in this work. The manifold is shown in Fig. 1. A Tokyo Rikakikai Model MP-3 two-channel variable-speed peristaltic pump was used with Tygon tubes for the sample and buffer transferences. A

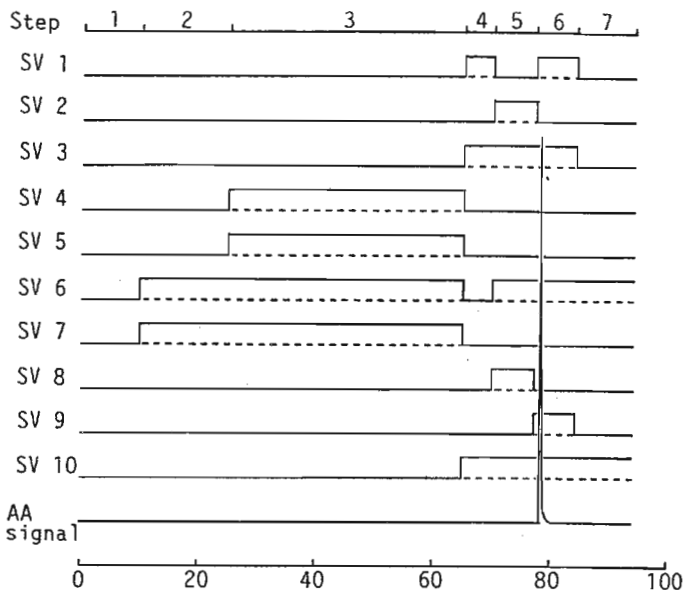


Fig. 2 Operation of the three-way solenoid valves for the on-line preconcentration system. Step 1, conditioning; step 2, sampling; step 3, concentration; step 4 and 5, segmentation by air; step 6, elution; step 7, return to initial state.

Sanuki Kogyo syringe pump was used for both the sample uptake and the elution of copper(II) from the oxine-AC column. Ten Model MTV-31 three-way solenoid valves (Takasago Denki) and two three-way joints were used. The other parts of the suction-flow injection system were connected with 1-mm i.d. Teflon tubing. The loading (preconcentration) and elution periods were governed by setting program which controlled the operation of the solenoid valves (Fig. 2). Compressed-air was utilized for segmentation and extrusion of the eluent.

Double-vessel digestion bombs were used for the decomposition of steel and biological samples.¹⁵

Procedure

A sample solution (pH 2.5-6; 10 cm³) is sucked up through Teflon tube by the syringe pump and is merged into the buffer line and mixed. Copper(II) ions are retained and concentrated on the oxine-AC column while the buffer

solution is continuously passed through the column and introduced into the nebulizer of the spectrometer except elution procedure. Then water is sucked up for rinsing followed by segmentation which is proceeded by compressed-air at a pressure of 0.4 kg cm^{-2} in order to remove the rinse water. Finally, the eluent (4 mol dm^{-3} nitric acid) is sucked up and subsequently extruded at a flow-rate of $9.0 \text{ cm}^3 \text{ min}^{-1}$ with a 0.2 kg cm^{-2} of compressed-air to elute the collected ions. Table 1 Recommended operating conditions

The transient absorption signal is recorded on a strip-chart recorder and the peak height is measured.

All the steps are carried out automatically.

The recommended operating conditions are summarized in Table 1.

Suction-flow injection system	
Sample volume	10 cm^3
Buffer solution	0.05 mol dm^{-3} (pH 3) Ammonium citrate
Eluent	4 mol dm^{-3} HNO_3
Column size	$2 \text{ mm i.d.} \times 10 \text{ cm}$
Air pressure	0.2 kg cm^{-2}
AA spectrometer (Shimadzu AA-610S)	
Analytical line	324.8 nm
Air	$10 \text{ dm}^3 \text{ min}^{-1}$
Acetylene	$2 \text{ dm}^3 \text{ min}^{-1}$
Recorder range	50 mV/full scale

RESULTS AND DISCUSSION

Optimization of operating conditions

The AC for gas chromatography chosen in this work showed a high adsorption activity together with a low back-pressure and minimum copper blank, since it has a porous, coarse (80-100 mesh) structure, and is highly pure. Such features were very favorable for the on-line sample introduction system.

The effect of column size on the copper signal was investigated while keeping the loaded amount of copper(II) at 100 ng . With a column of 2.0 mm i.d. , the sharpest and highest peaks were obtained. Using a column wider than 2.0 mm i.d. lowered the copper signal. Diffusion upon the elution of copper(II) seems to have caused this result. Regarding the column length, a minimum length of 5 cm was

necessary for a complete collection of copper(II). A column longer than 20 cm produced extra back-pressure and disturbed the constant flow. When using a column of less than 5 cm length, copper(II) could not be retained completely. Therefore, an optimum 10-cm column length was chosen and used throughout this work.

Nitric acid was used as an eluent; a maximum, constant absorption of copper was obtained in the range from 2.0 to 4.0 mol dm⁻³. In this work, 4.0 mol dm⁻³ of nitric acid was used for the elution of copper(II) throughout. Under the above mentioned conditions, we confirmed that the constructed column could be used for the analysis of at least 60-replicates without any reloading with oxine, when 10 cm³ of a standard solution containing 100 ng cm⁻³ copper(II) was introduced into the system each time.

In order to evaluate the pH response of the oxine-AC column, the pH of a sample solution containing 100 ng cm⁻³ copper(II) was varied by adding dilute nitric acid or dilute ammonia water. The analysis was then carried out under the recommended conditions in which the pH of the 0.05 mol dm⁻³ diammonium hydrogen citrate buffer solution was adjusted to 3 with 1 mol dm⁻³ nitric acid. The results are presented in Fig. 3. When the pH of the sample solution was less than 2.5, a fraction of copper(II) broke through the column. Therefore, the pH of a sample should be adjusted to be between 2.5 and 6 prior to analysis by adding citric acid or ammonia water.

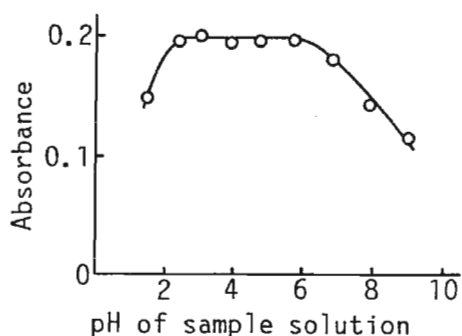


Fig. 3 Effect of pH of sample solution on atomic absorption of copper. Buffer solution, 0.05 mol dm⁻³ ammonium citrate (pH 3); copper(II), 100 ng cm⁻³.

As Fig. 4 shows, the pH of the buffer solution should be in the range of 2 - 8 when a sample solution of pH 3 is

introduced into the system. Furthermore, citrate and acetate buffer solutions gave almost similar responses in the tested pH range of 1 - 11. It was desirable to keep the pH of the buffer solution as low as possible to avoid adsorption of foreign ions and precipitation of metal hydroxide. Consequently, 0.05 mol dm⁻³ of citrate buffer (pH 3) was used throughout this work.

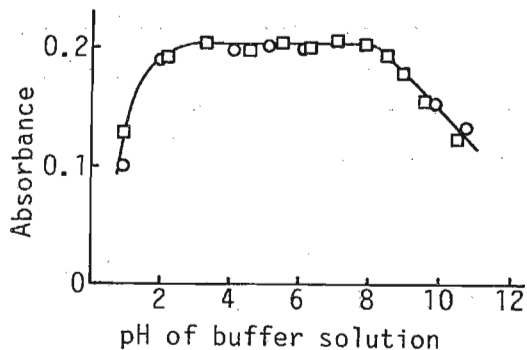


Fig. 4 Effect of pH of buffer solution on atomic absorption of copper.
 ○, 0.05 mol dm⁻³ ammonium citrate;
 □, 0.5 mol dm⁻³ ammonium acetate;
 copper(II), 100 ng cm⁻³ (pH 3).

Calibration and precision

Under the recommended conditions, the detection limit (3σ) was 4.4 ng cm⁻³. The sensitivity and detection limit were both one order of magnitude better than those obtained by direct aspiration of the aqueous solution. The calibration graph for copper was linear up to 0.3 μg cm⁻³, and the relative standard deviation for 5 replicate measurements of 0.1 μg cm⁻³ copper was 2.0%. Twenty samples could be analyzed per hour.

Interference

The effects of foreign ions which could make oxine-complexes easily in weak acidic media (pH 3) were investigated by using each solution containing 100 ng of copper(II). Tolerable amounts of foreign ions, which gave less than a 10% error for the determination of copper(II), were evaluated. The maximum concentration examined was 1000-times the concentration of

Table 2 Permissible amounts of foreign ions for the determination of copper (results within 10% error)

Ion	Maximum permissible weight ratio ^a
V(V)	900
Ni(II)	900
Nb(V)	300

The following species were tolerated at a 1000:1 ratio: Al(III), Fe(III), Mo(VI), Ga(III).
^aCu(II), 100 ng cm⁻³.

copper(II) by weight. Within the concentration ratio, foreign ions such as aluminium(III), iron(III), molybdenum(VI) and gallium(III) produced no interference. Tolerable amounts of interfering ions are given in Table 2. These tolerance limits would allow the determination of copper in most environmental and steel samples without interference by foreign ions.

Application to practical samples

The accuracy of the method was confirmed by analyzing NBS standard and NIES certified reference materials. The Vehicle Exhaust Particulate contains siliceous and carbonous materials. In order to achieve complete dissolution of the material, the sample was digested with a mixture of nitric/perchloric/hydrofluoric acids at around 200°C in a Teflon beaker. As for the other samples, a decomposition procedure using double-vessel digestion bombs was selected from the literature.¹⁵ The results shown in Table 3 are in good agreement with the certified values. Therefore, the proposed method can be successfully applied to the determination of copper in such types of samples.

Table 3 Determination of Copper in certified reference materials

Sample	Copper/ $\mu\text{g g}^{-1}$	
	Found ^a	Certified
Pepperbush (NIES CRM No.1)	12.3 \pm 1.3	12 \pm 1
Pond Sediment (NIES CRM No.2)	218 \pm 14	210 \pm 12
Vehicle Exhaust Particulates (NIES CRM No.8)	62.9 \pm 2.0	67 \pm 3
Low Alloy Steel (NBS SRM 362)	4900 \pm 100	5000
Orchard Leaves (NBS SRM 1571)	9.9 \pm 1.0	12 \pm 1

^aMean \pm ave. dev., 3 results.

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