



Online determination of copper in aluminum alloy by microchip solvent extraction using isotope dilution ICP-MS method

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ABSTRACT

Isotope dilution mass spectroscopy (IDMS)/ICP-MS combined with microchip solvent extraction was successfully applied for the online determination of copper in an aluminum alloy. The microchip solvent extraction was developed for the separation of Cu from major element, and optimal pH range was wider than that of the batchwise extraction method. The dimensions of the microchip were 30 mm × 70 mm and that of micro-channel on the microchip was 180 μm wide and 40 μm deep. The copper complex with 8-hydroxyquinoline was extracted into *o*-xylene at pH 5.5 and back extracted with 0.1 mol l⁻¹ nitric acid at flow rate of 20 μl min⁻¹. The total extraction efficiency (water/organic solvent/nitric acid) was around 40%. IDMS/ICP-MS was coupled with solvent extraction for precise determination of Cu. The extraction and back-extraction on the microchip took about 1 s and the total measurement time for the IDMS/ICP-MS was about 40 s/sample. The blank value of this method was 0.1 ng g⁻¹. The proposed method was used for the determination of Cu in Al standard materials (JSAC 0121-C, The Japan Society for Analytical Chemistry and 7074 Al alloy, Nippon Light Metal Co. Ltd.). The obtained analytical results are in good agreement with the certified values.

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1. Introduction

Aluminum is one of the abundant elements and widely used as alloys. The precise determination of impurities in highly purified Al alloys is very important especially for use in electronic devices. Copper is one of the major impurities included in Al alloys, but it is difficult to determine the low concentration of Cu in Al alloys without any pretreatment. When the concentration of the target element is very low, inductively coupled plasma-mass spectrometry (ICP-MS) is a useful instrument. When the metal matrix, such as Al coexists in a large quantity, it causes damage to the quadrupole detector of the ICP-MS [1]. The matrix destabilizes the ionization efficiency of the plasma and matching the calibration standard solution is difficult for the ICP-MS measurement because of high Al concentration. Furthermore, the isobars of a large quantity of Al origins (²⁷Al³⁶Ar and ²⁷Al³⁸Ar) interfere with the detection of ⁶³Cu and ⁶⁵Cu. Therefore, Cu has to be separated from the Al matrix.

Various pretreatment methods for the determination of Cu in an Al matrix have been reported, such as solvent extraction [2], solid-phase extraction [3] and ion-exchange separation methods [4], etc. However, these methods are complicated and require much time for the determination. In general by using conventional solvent

extraction methods, large amounts of organic solvents are wasted. Therefore, these methods are always necessary to examine about detailed recovery of the purpose elements.

The electrolytic dissolution of an Al alloy and determination of metals by inductively coupled plasma-optical emission spectrometry (ICP-OES) was reported [5]. This method is relatively fast (about 30 min). However, the limit of detection (LOD) of Cu is high (0.047 μg ml⁻¹).

As the direct method for a solid sample, glow discharge-mass spectrometry is possible to high sensitive measurement [6,7]. However, it is necessary to obtain a relative sensitivity factor for each sample to get reliable date.

The microchip method has attracted much attention, because it enables chemical process to miniaturize. The microchip has been used for various purposes such as chemical synthesis, immunoassay, etc [8,9]. Recently microchip method has various advantages in the analytical field, such as speed, easiness for automation, and small amounts of sample and waste solutions [10–15]. This method also provides advantages in solvent extraction, such as a large interfacial area/volume ratio, short diffusion distance and stable measurement of laminar flow [16].

The mass transfer process at the interface between the aqueous and organic phases in the micro-channel was reported [17]. Yttrium was separated from Zn by the difference in the extraction rates in the micro-channel of the two-phase flow and three-phase flow [18,19]. However, the extraction efficiency did not reach 100%

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in many cases because the contact time of the water and organic phases was limited (usually second-order) on the microchip. Lower extraction efficiency needs higher sensitivity for the detection, but microchip extraction is useful for the separation from the matrix.

The thermal lens microscope (TLM) combined with the microchip solvent extraction (two or three-layer flow system) was used for the online determination of uranium, nickel, cobalt, etc [20–25]. This method is a highly sensitive for nonfluorescent molecules, widely used for the detection on a microchip and the total measurement time is very fast. However, TLM does not have a metal selectivity in order to measure the fluctuation of the TL signal intensity and the precision depends on the extraction rate on the microchip.

Among calibration methods, isotope dilution mass spectroscopy (IDMS) can be suitable for the precise determination when it is used with the microchip method. IDMS does not require any quantitative extraction because the isotope ratio of an element, which is determined as the internal standard, is used. IDMS can selectively determine a metal ion and can measure many metallic elements at the same time. It was reported that five metal ions were measured at the same time with IDMS [26]. Moreover, IDMS is used as the primary standard method with good precision [27,28]. The measurement procedure of IDMS requires only the weight of the sample and the spiked IDMS solution [29].

In this study, we developed the online determination system of Cu in an Al alloy, in which a microchip was used for the solvent extraction and directly connected to the ICP-MS. In the microchip, Cu was selectively extracted with 8-hydroxyquinolin into the organic phase (*o*-xylene), and then back-extracted into the acid solution. Moreover, the pH range, in which Cu could be separately extracted from Al, was wider than that of the batchwise extraction method. The back extracted Cu was directly determined by IDMS. IDMS has a superior characteristic that the detectable value does not depend on the extraction rate of the microchip. Under the optimized conditions, the observed value of the standard materials agreed well with the certified value. The estimated contact time in the micro-channel was about 1 s and the total IDMS measurement time was about 40 s/sample. The amount of the sample and organic solvent for one analysis were about 10 μ l each. 8-Hydroxyquinoline and *o*-xylene are effectively used for Cu extraction [30,31]. Microchip can be reused and was not polluted by metals if washed by sodium hydroxide, Milli-Q water and nitric acid.

2. Experimental

2.1. Reagents

8-Hydroxyquinolin (8-HQ, Kanto Chemical Co., Inc., Tokyo, Japan) and *o*-xylene (Kanto Chemical Co., Inc.) were analytical reagent grade, and ultrapure grades of ammonia water, acetic acid, hydrochloric acid and nitric acid (Ultrapure, Kanto Chemical Co., Inc.) were used. The mixture of the metal standard solution (10 mg l⁻¹, Al, Ca, Cu, K, Mg, Na, Ni, Ti and Zn, Plasma CAL-Multi-Element Standard, SCP SCIENCE) and the single metal standard solution (1000 mg l⁻¹, Al, Cu, AAS grade, Wako Pure Chemicals, Osaka, Japan) were used as received. For the IDMS, 10 mg kg⁻¹ Cu-65 (Merck Ltd., Darmstadt, Germany) was used. The isotope ratio of the spiked Cu is ⁶³Cu:⁶⁵Cu = 0.002926:0.997974. The aluminum alloy, JSAC 0121-C (The Japan Society for Analytical Chemistry, Tokyo, Japan) and 7074 Al alloy (Nippon Light Metal Co. Ltd., Shizuoka, Japan), was used as the certified standard material: certification value of Cu was 3.48 ± 0.11 μ g g⁻¹ and 0.009 (w/w)%, respectively.

Table 1
Operating conditions of HR-ICP-MS.

| | |
|--|----------------------------|
| Instrument setting | |
| RF power (kW) | 1.3 |
| Coolant gas flow rate (l min ⁻¹) | 17 |
| Auxiliary gas flow rate (l min ⁻¹) | 0.5 |
| Sample gas flow rate (l min ⁻¹) | 1.4 |
| Sampling cone | Pt (1.0 mm i.d.) |
| Skimmer cone | Pt (0.7 mm i.d.) |
| Nebulizer | PTFE 20 μ l/min |
| Spray Chamber | PTFE Scott-type |
| Measurement parameters | |
| Resolution | 300 (Low) |
| Scan type | E-scan |
| Detector mode | Both (Counting and Analog) |
| Mass window (%) | 5 |
| Sample time (s) | 0.01 |
| Sample per peak | 100 |
| Run (times) | 4 |
| Pass (times) | 100 |
| Total time (s) | 40 |

2.2. Instruments

A high resolution ICP-MS (HR-ICP-MS, ELEMENT2, Thermo Fisher Scientific, Bremen, Germany) equipped with a 20 μ l min⁻¹ microflow nebulizer (Elemental Scientific Inc., Omaha, USA) was used for the determination of the element concentrations. The operating conditions of the HR-ICP-MS are summarized in Table 1. ICP-OES (Vista-PRO, SII Nano Technology Inc., Tokyo, Japan) was used for the extraction efficiency experiment. The aluminum alloy was decomposed by a microwave (ETHOSTC, Milestone s.r.l., Sorisole, Italy).

2.3. Microchip for solvent extraction

Fig. 1 shows the layout and dimensions of the micro-channel (Institute of Microchemical Technology, Kanagawa, Japan) carved on a glass plate (30 mm × 70 mm) in which the extraction and back-extraction experiments were carried out. The micro-channel was typically 180 μ m wide and 40 μ m deep. The guide depth of 20 μ m in the micro-channel allowed two individual stable flow lines. Single syringe pump C (pump 11, Harvard Apparatus, MA, USA) and dual syringe pumps A and B (pump 33, Harvard Apparatus) were used for injection of the solutions into the microchip. All the syringes are metal-free syringes (LT type, 5.0 ml, Hamilton). The total system (all syringes, connection tubes, connecting parts and microchip) was boiled in dilute nitric acid for more than one hour just before use. The microchip was washed with 1 mol l⁻¹ sodium hydroxide, Milli-Q water and 1 mol l⁻¹ nitric acid for more than one hour just before use. The stable flow was observed with a microscope. The aqueous and organic solutions were injected into the microchip by syringe pumps A and B, respectively, and the flow rates of these solutions were 20 μ l min⁻¹. The effluent from the microchip flowed directly into the microflow nebulizer of the HR-ICP-MS via the PEEK tube (0.26 mm i.d., 0.5 mm o.d.): the flow rate of the microflow nebulizer was 20 μ l min⁻¹.

The sample solution was injected into a microchip by syringe A and the organic solution (0.05 (w/w)% 8-HQ in *o*-xylene) was injected by syringe B. At the first merging point, solvent extraction was carried out. After the extraction, the organic phase containing metal-chelate complex was pumped to the second merging point. The organic phase was mixed with nitric acid which was injected by syringe C and back-extraction occurred here. Finally, the effluent was introduced to HR-ICP-MS on-line. All measurements were performed at 23 °C in the controlled room.

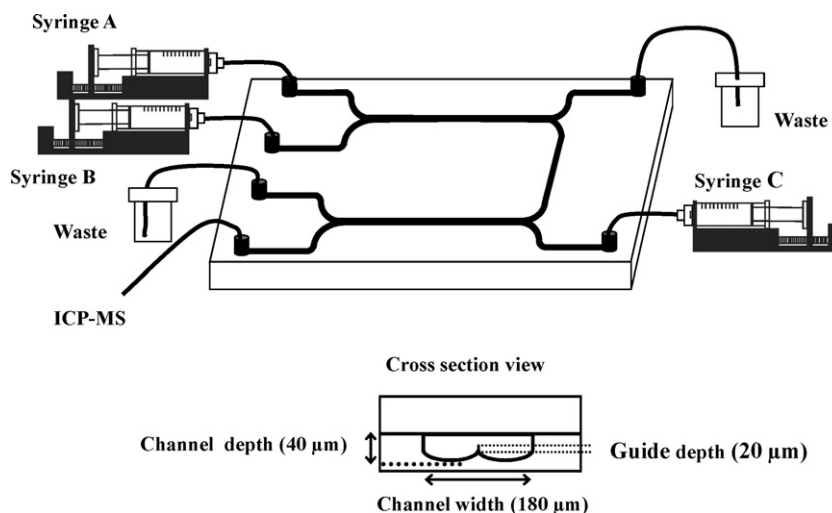


Fig. 1. The microchip extraction system.

2.4. Preparation of sample solution

Twenty milligram of the Al alloy sample were added a tetrafluoromethaxil (TFM) vessel containing 0.3 g of hydrochloric acid, 0.1 g of nitric acid and 8.0 g of Milli-Q water. Then 20 mg of the Cu spiked reagent for the IDMS were added. The microwave digestion program was set at 220 °C for 30 min. After the digestion, ammonium acetate buffer was added to adjust the pH to 6.0 and diluted up to 50 g with Milli-Q water. All solutions were filtered through a 0.45 μm pore size polytetrafluoroethylene (PTFE) filter for eliminating any solid substances before introduction into the microchip.

3. Results and discussion

3.1. Extraction conditions for metal ions with 8-HQ

The pH dependence of the Al extraction efficiency with the microchip was examined using 400 mg l⁻¹ Al solution which was calculated from the procedure in 2.4. The extraction efficiency was examined in the pH range from 3.5 to 6.0. The experiment was carried out with the upper channel of the microchip system shown in Fig. 1: sample solution of Al (C_{init}) and *o*-xylene phase containing 0.5 (w/w)% 8-HQ were first pumped at the flow rate of 20 μl min⁻¹ and the aqueous phase (“waste” as shown in Fig. 1) after extraction was collected. The contact time of the interface of microchip was about 0.5 s at this flow rate. The concentration of the aqueous phase (waste, C_{waste}) was then determined by ICP-OES using the external calibration method. The extraction efficiency was calculated with Eq. (1).

$$\text{The extraction coefficient (\%)} = \frac{(C_{init} - C_{waste})}{C_{init}} \times 100 \quad (1)$$

Aluminum (400 mg l⁻¹) was not extracted in the pH range from 3.5 to 6.0. In the batchwise extraction method, Al was extracted in the pH range from 4.5. Therefore, the effect of Al concentration was examined with a practical concentration range of the analysis from 0.4 to 40 mg l⁻¹ at pH 5.5. As a result, aluminum was not extracted in these concentration ranges.

The pH dependence of the extraction efficiencies of the mixture metal solution (Al and Cu) with the microchip was examined with 0.2 mg l⁻¹ metals solution. The extraction efficiency was examined in the pH range from 2.5 to 7.0. The results about Al and Cu are shown in Fig. 2. Copper was extracted about 30% at the range from pH 2.5 to 3.5 and about 80% in the range from pH 4.0 to 6.0 in which

the extraction efficiency of Al was almost 0%. In this pH range, the selective extraction of Cu from Al with sufficient extraction efficiency was achieved; the pH of the sample solution was therefore adjusted to 5.5. This pH range is wider than that of the batchwise extraction method in which the pH range is about 2.5–4.0. This difference may be attributed to the difference in the extraction rate of the Al ion and Cu ion with 8-HQ in the time scale of 0.5 s. The extraction constants ($\log K_{ex}$) of Cu and Al with 0.1 mol l⁻¹ 8-HQ into CHCl₃ were reported as 1.77 and -5.22, respectively [32,33], which was expected that Cu was faster to extract into *o*-xylene with 8-HQ faster than Al. In this study, we used *o*-xylene because chloroform is not recommended due to the environmental pollution and health for an operator.

The effect of the Cu concentration is also an important factor. The extraction efficiency of Cu was examined with 0.01 to 1.0 mg l⁻¹ of Cu solutions at pH 5.5. About 80% of the copper was extracted in this concentration range.

In Al alloy, other elements which form an isobar of copper as well as Al interfere with the determination of Cu. The interference was examined using the mixed metal standard solution. The extraction efficiencies containing each 0.2 mg l⁻¹ were also obtained with Eq. (1). Calcium, potassium, magnesium, sodium, nickel and zinc were not extracted in the pH range from 2.5 to 7.0.

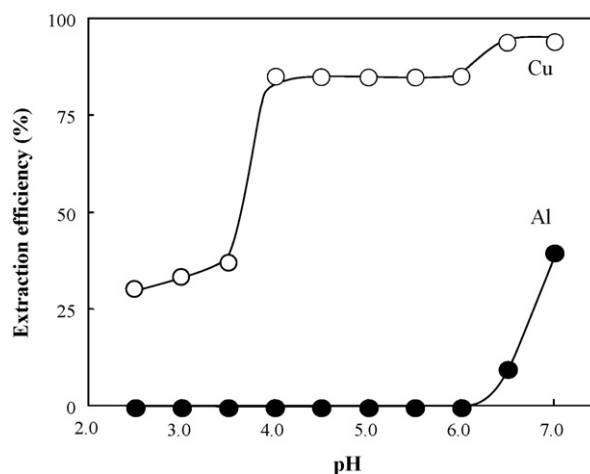


Fig. 2. Effect of pH on the extraction efficiency of Cu and Al by the microchip solvent extraction method. Copper and Aluminum: 0.2 mg l⁻¹ (pH 2.5–7.0); 8-HQ: 0.5 × 10⁻¹ (w/w)%.

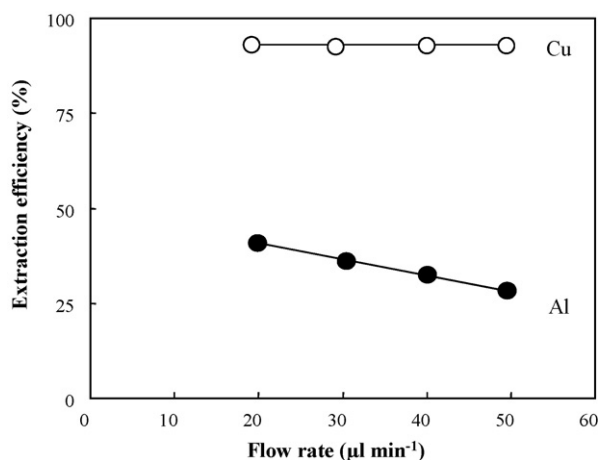


Fig. 3. Effect of flow rate on the extraction efficiency of Cu and Al by the microchip solvent extraction method. Copper and Aluminum: 0.2 mg l⁻¹ (pH 7.0); 8-HQ: 0.5 × 10⁻¹ (w/w)%.

About 40% of the titanium was extracted in the pH range from 5.5 to 7.0.

The effect of contact time of the two phases on the extraction efficiency of Al and Cu was examined by changing the flow rates of the water and organic phase. The result is shown in Fig. 3. In this experiment, the pH of the sample solution was adjusted to 7.0 to compare the extraction behavior of Al with Cu. The flow rates of both phases were changed from 20 to 50 µl min⁻¹, which corresponded to the contact time from 0.45 to 0.18 s. As the flow rate increased (the contact time was shorter), the extraction efficiency of Al gradually decreased, on the contrary, that of Cu remained constant at about 90%. Because the complexing rate of Cu with 8-HQ is very fast, there was no difference in the extraction efficiency in the examined time scale (~0.5 s).

3.2. Back-extraction conditions for Cu-8-HQ complexes with nitric acid

The effect of the concentration of nitric acid on the back-extraction efficiency of Cu was examined. The result is shown in Fig. 4. The back-extraction efficiencies of the microchip were calculated as follows: the organic phase which contains the 0.2 mg l⁻¹ Cu-8-HQ complexes and nitric acid solution from 0.01 to 3.0 mol l⁻¹ were first pumped at the flow rate of 20 µl min⁻¹ in the micro-

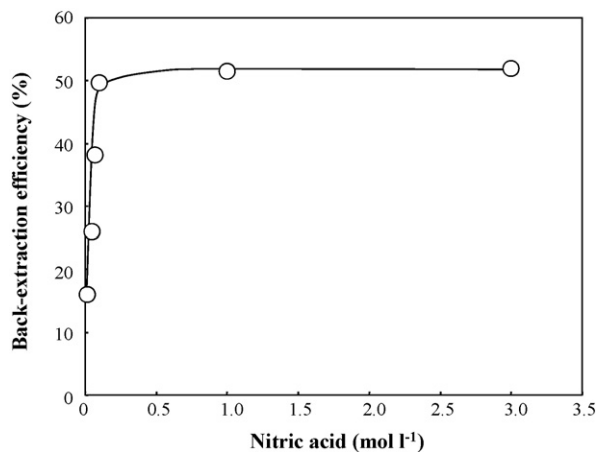


Fig. 4. Effect of nitric acid concentration on the back-extraction efficiency of Cu by the microchip solvent extraction method. Nitric acid: 0.01 to 3.0 mol l⁻¹; Cu-8-HQ complex: 0.2 mg l⁻¹.

channel in Fig. 1. The contact time of the two phases was about 0.5 s at this flow rate. The concentration of the aqueous phase (nitric acid phase) was then determined by ICP-OES using the external calibration method. As a result, the back-extraction efficiency of Cu was around 50% when the concentration of nitric acid was from 0.1 to 3.0 mol l⁻¹. There is the case that the precision of the ionic strength (cps) becomes worse when cps is over around 5,000,000 in HR-ICP-MS. However, this microchip solvent extraction method can easily control the extraction efficiency of the elements by changing the nitric acid concentration used for the back-extraction. This characteristic enabled the online measurement of a high concentration of Cu by adjusting the ionic strength below 5,000,000 cps. In this study, nitric acid concentration was kept at 0.1 mol l⁻¹ because the cps was not over 5,000,000.

The flow rate of the nitric acid solution was kept constant at 20 µl min⁻¹ adjusting to the flow rate of the microflow nebulizer of the ICP-MS. Subsequently, the overall extraction efficiency (extraction and back-extraction) of Cu was around 40% in the range of pH 4.0–7.0.

The back-extraction efficiency of Ti was also examined. As a result, it was about 10% when the concentration of the nitric acid is from 0.1 to 3.0 mol l⁻¹.

3.3. Determination with IDMS

Copper could be separated from Al by the above microchip extraction method, but the total extraction efficiency was not good at 40%. To increase the precision and reproducibility, we selected IDMS. IDMS is the primary standard method which can independently determine the recovery [34,35]. The equation for the IDMS calculation is as follows:

$$C = \frac{C_{\text{spike}} \times M_{\text{spike}}}{M_{\text{sample}}} \times \frac{[(a_{\text{spike}}^1 - a_{\text{spike}}^2 \times R_{\text{meas}})]}{(a_{\text{sample}}^2 \times R_{\text{meas}} - a_{\text{sample}}^1)} \times R_{\text{ATW}}$$

where C , C_{spike} , M_{spike} , M_{sample} , a_{spike}^1 , a_{spike}^2 , R_{meas} , a_{sample}^2 , a_{sample}^1 and R_{ATW} are the concentration of Cu in the sample, concentration of Cu spiked solution, mass of spiked Cu, mass of Cu in the sample, abundance of spiked isotope ⁶³Cu ($^{63}\text{Cu}_{\text{spike}}/\text{Cu}_{\text{spike}}$), abundance of spiked isotope ⁶⁵Cu ($^{65}\text{Cu}_{\text{spike}}/\text{Cu}_{\text{spike}}$), measured isotope ratio ($^{63}\text{Cu}_{\text{blend of sample and spike}}/^{65}\text{Cu}_{\text{blend of sample and spike}}$), abundance of isotope ⁶⁵Cu in the sample ($^{65}\text{Cu}_{\text{sample}}/\text{Cu}_{\text{sample}}$), abundance of isotope ⁶³Cu in the sample ($^{63}\text{Cu}_{\text{sample}}/\text{Cu}_{\text{sample}}$) and ratio of atomic weights ($\text{Cu}_{\text{sample}}/\text{Cu}_{\text{spike}}$), respectively.

For the IDMS, it is necessary to completely remove the interferences from the isobar for measuring the accurate isotope ratio of the target element. When the interference cannot be experimentally eliminated, the spectrum interference correction of the spectrum should be done [36]. In this microchip extraction method, the interference element, such as Al, could be eliminated before the measurement.

Generally, the isotope ratio, which is measured by ICP-MS, is different from the reported value of The International Union of Pure and Applied Chemistry (IUPAC) [37]. This seems to be due to the mass discrimination effect in the ICP-MS [38,39]. In this study, the mass discrimination correction was done by multiplying the correction coefficient which was determined by the Cu isotope ratio from the IUPAC and the isotope ratio measured by the Cu standard solution [40–42]. The isotopic fractionation effect [43], which might occur during the extraction process, could be neglected. The most suitable amount of the spike ratio of ⁶⁵Cu/⁶³Cu was calculated from the error multiplication factor [26,44,45]. In this study, the spike solution was added to the sample solution so that the ⁶⁵Cu/⁶³Cu ratio was estimated to be about 10.

Table 2
Analytical results of copper in aluminum alloy certified reference materials.

| Sample | Found | | Certified value |
|---------------|--------------------------------|--------------------------------|--------------------------------|
| | Batchwise extraction | This method | |
| JSAC 0121-C | 3.70 ± 0.03 μg g ⁻¹ | 3.46 ± 0.01 μg g ⁻¹ | 3.48 ± 0.11 μg g ⁻¹ |
| 7074 Al alloy | 0.0089 ± 0.0001 (w/w)% | 0.0089 ± 0.0001 (w/w)% | 0.009 (w/w)% |

n = 5.

3.4. Interferences

The analytical results obtained by the batchwise separating funnel method was relatively high compared with that of the microchip method. This may be caused from the isobars of Al, because 8-HQ also extracts Al at pH 5.5. In the Al alloy, Si, Mg and Ti are included which seem to interfere with the determination of Cu. The interference from Si and Mg, however, could be neglected because these elements were hardly extracted with 8-HQ in *o*-xylene. On the other hand, the content of Ti in JSAC 0121-C is half that of Cu, whereas the certified value of Ti in the 7074 Al alloy is not shown. The concentration of Ti was determined by ICP-OES: it was a quarter of that of Cu. The extraction efficiency of Ti was about 40% at pH 5.5 by the microchip method, and the back-extraction efficiency of Ti was about 10%. The interference isobars which affect the determination of Cu are ⁴⁷Ti and ⁴⁹Ti and these contents were calculated to be 7.3% and 5.5% of the initial Ti concentration, respectively. As a result, the effect of Ti could also be neglected. The blank value of this microchip method was 0.1 ng g⁻¹ which did not affect the measurement of the JSAC 0121-C and the 7074 Al alloy.

3.5. Application to Al alloy

Table 2 shows the analytical results of Cu in the certified standard materials (JSAC 0121-C and 7074 Al alloy) compared to those of the batchwise extraction method. The total measurement time was less than 1 min/sample. While the batchwise extraction method takes 60 min for the separating funnels shaking at 200 times min⁻¹. This microchip extraction method of the JSAC 0121-C and the 7074 Al alloy provide good agreement with the certified value. The analytical results for the batchwise and the microchip results of the 7074 Al alloy were both in agreement with the certified value. However, the result with batchwise extraction method of JSAC 0121-C was higher than the range of uncertainty for the certified value. JSAC 0121-C has a low Cu concentration comparison for the 7074 Al alloy. It is postulated that the analysis of JSAC 0121-C was more affected by the isobars of a large quantity of Al (²⁷Al³⁶Ar and ²⁷Al³⁸Ar) than that of the 7074 Al alloy. These analytical results showed that the microchip method was especially effective when the Cu content in the Al alloy is quit low.

4. Conclusion

We established a fast and accurate online analysis system of trace Cu in an Al alloy, in which the solvent extraction/back-extraction method in the microchip could separate Cu from the matrix element, Al, and IDMS was adopted to provide a good accuracy and precision of the determination, regardless of the microchip solvent extraction efficiency was about 40%. The total measurement time was less than 1 min and the sample volume was only 10 μl for one sample analysis. Moreover, the pH range, in which Cu could be separately extracted from Al, was wider than that of the batchwise extraction method. This wider pH range may be use-

ful when this system is applied to other samples under optimized conditions.

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