A sensitive and selective method for determination of gold(III) based on electrothermal atomic absorption spectrometry in combination with dispersive liquid-liquid microextration using dicyclohexylamine

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Abstract

A combined method with dispersive liquid-liquid microextraction (DLLME) and electrothermal atomic absorption spectrometry (ETAAS) has been developed for determining gold(III). Dicyclohexylamine, a new extractant for gold(III), showed excellent performance in DLLME. Acetone was indispensable to the quantitative extraction of gold(III), contributing to decrease in hydration, decrease in the difference in the dielectric constants between the supernatant phase and the sedimented phase, and dissolution of a part of chloroform as an extraction solvent to the supernatant phase as well as improvement of dipersibility. In DLLME using a mixture of 1.0 mL of acetone and 100 µL of chloroform containing 50 mmol L^{-1} of dicyclohexylamine, gold(III) could be extracted selectively and effectively from 8 mL of a sample solution in the presence of iron(III), cobalt(II), nickel(II), copper(II), palladium(II), and platinum(IV) at pH 1. The extracted gold(III) was determinable by ETAAS; the detection limit was 0.002 µg L^{-1} (three times the standard deviation of the blank values, n=8) as a gold(III) concentration in 8 mL of sample solution. The proposed method was applicable to the determination of gold in platinum metal and its alloy as well as effluent without any interference by the matrices.

1. Introduction

Gold, which has important characteristics such as high ductility, corrosion resistance, low impedance, and catalytic properties, is widely utilized in the electronic, electroplating, fine-chemical, and jewelry industries [1].   Because it is precious, gold is carefully recovered after use through various techniques such as electrolysis and ion exchange [2,3]; however, complete recovery cannot be achieved, and a small amount of gold is lost through routes such as effluents. To estimate the amount of gold lost through an effluent, a method in which gold can be sensitively determined without any interference by the major ions generally contained in the effluent is necessary.

Other precious metals, including platinum, are also key materials for various industries [1].   With the expansion of its applications, such as in fuel cells, a growing demand for high-purity platinum is expected [4,5].   Because platinum metal contains significant impurities, including gold, an accurate and precise method of analysis is required.

For the determination of gold, electrothermal atomic absorption spectrometry (ETAAS) is a powerful tool [6]; however, the sensitivity is sometimes insufficient and the presence of matrices seriously interferes with the analyses of effluents, metals, and alloys.   Therefore, a separation and preconcentration technique is extensively applied to the ETAAS determination of gold [6].

Liquid-liquid extraction (LLE) is an effective method for the separation and

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preconcentration of gold(III) [7-12].   Amine compounds, including *n*-trioctylamine [9], *n*-octylaniline [10], *N*-phenylbenzylamine [11], and *N*-*n*-octylaniline [12], are conveniently utilized for the extraction of gold(III) and other elements.   However, there are some problems with the use of LLE, including the large amounts of harmful organic solvents needed, the long extraction time required for quantitative extraction, and difficulty in the treatment of wastewater generated after extraction.

To overcome these problems, various types of LLE techniques have been proposed. Among them, microextraction techniques have been investigated intensely.   Homogeneous liquid-liquid extraction (HoLLE) based on a ternary solvent system [13-17] is one of the most useful microextraction techniques.   HoLLE utilizes the phase separation phenomenon from a homogeneous solution, and the analytes are rapidly and efficiently extracted into a separated phase. HoLLE is available for the separation and preconcentration of some elements [14-17], but there has been no report on the separation and preconcentration of gold(III).   Dispersive liquid-liquid microextraction (DLLME) [18] has also attracted attention recently [19-27].   In DLLME, as in HoLLE, an aqueous sample solution, a water-miscible organic solvent as the disperser solvent, and a water-immiscible organic solvent as the extraction solvent are used; however, the extraction solvent has only to disperse finely into solution.   In general, a mixture of disperser solvent and extraction solvent is swiftly injected using a microsyringe, and a gentle shaking is applied to extract

the analyte quantitatively into the dispersed extraction solvent. The selection of a dispersive solvent which gives favorable dispersibility of the extraction solvent is important to achieve effective extraction of analyte [18-27]. DLLME is conveniently applicable to the separation and preconcentration of various elements prior to their ETAAS determination [19-27]; for gold(III), however, only DLLME using victoria blue R has been reported [25].

In this work, we investigated a combined method with DLLME and ETAAS for determining gold(III). For DLLME using acetone as a water-miscible organic solvent and chloroform as a water-immiscible organic solvent, we tested 11 kinds of amine compounds as extractants and found that dicyclohexylamine, which has not been used for the extraction of gold(III), was excellent. It is noteworthy that DLLME using dicyclohexylamine has rather high selectivity; gold(III) could be determined by ETAAS without any interference even in the presence of large amounts of other elements. In this paper, we report the results of investigations of the DLLME of gold(III) with amine compounds and discuss the role of acetone as a water-miscible organic solvent in the extraction of gold(III) with dicyclohexylamine. The potential of ETAAS combined with DLLME using dicyclohexylamine is also demonstrated through the determination of gold in effluent, platinum metal, and platinum alloy.

2. **Experimental**

2.1   Apparatus

A Hitachi 180-80 polarized Zeeman atomic absorption spectrometer (flame- and electrothermal-type) was used to measure gold and other elements.   The pH measurement and ultrasonic irradiation were carried out using a Horiba F-22 pH meter and an AS ONE US-2 ultrasonic cleaner (120 W, 38 kHz), respectively.   A Kubota Model 5400 centrifuge was used to form the sedimented phase.

2.2   Reagents

Purified water obtained by a Simplicity UV (Millipore) was used for all experiments. Standard solutions of gold(III) and the other elements (1000 mg L^{-1}) were purchased from Kanto Chemical.   Eleven kinds of amine compounds, ethylenediamine (guaranteed reagent grade, GR, Wako Pure Chemical Industries), diethylenetriamine (GR, Wako Pure Chemical Industries), *N*-butyldimethylamine (>98%, Tokyo Chemical Industry), triphenylamine (GR, Kanto Chemical), *N*-methyldiphenylamine (97%, Acros Organics), *N*-methylaniline (GR, Kanto Chemical), *N*-phenylbenzylamine (99%, Acros Organics), benzylamine (GR, Kanto Chemical), dibenzylamine (>97%, Tokyo Chemical Industry), cyclohexylamine (>99%, Tokyo Chemical Industry), and dicyclohexylamine (>99%, Tokyo Chemical Industry), were used as extractants without any further

purification (the structures are summarized in **Fig. 1S** in the Supplementary Material).   The other

reagents, including chloroform, acetone, hydrochloric acid, and sodium hydroxide, were of GR or

analytical reagent grade.

2.3   Procedures

2.3.1   Extraction behavior of gold(III) with some amine compounds

As a test solution, 0.1 mol L^{-1} hydrochloric acid spiked with gold(III) (4 mg L^{-1} or 10 μg

L^{-1}) was used.

For DLLME, the test solution (5 mL) was taken into a 10 mL glass centrifuge tube.   To

the solution, a mixture of 0.90 mL of acetone and 90 μL of chloroform containing 50 or 200 mmol

L^{-1} of amine compound was swiftly injected using a glass syringe equipped with a stainless needle.

After the cloudy solution was gently shaken by hand for approximately 10 s, the solution was

centrifuged at 3000 rpm for 8 min.   Gold in the supernatant phase was determined using flame

atomic absorption spectrometry (FAAS) under the operating conditions shown in **Table 1**.   The

extraction percentage was calculated based on the initial amount of gold in the test solution and the

amount in the supernatant phase, which was calibrated using the supernatant phase spiked with an

appropriate amount of gold(III) after the blank test.

For LLE, 1 mL of chloroform containing 1-200 mmol L^{-1} of amine compounds and 0-10

mL of acetone was added to 50 mL of the test solution containing 4 mg L^{-1} of gold(III).   The

solution was then stirred vigorously.   The concentration of gold(III) in the supernatant solution

was measured using FAAS after centrifugation.   The extraction percentage was calculated in the

same manner for DLLME.

2.3.3   Determination of gold by ETAAS after DLLME using dicyclohexylamine

For the optimization of the extraction conditions, a purified water-based solution

containing 10 µg L^{-1} or 0.2 µg L^{-1} of gold(III), in which the pH was adjusted using hydrochloric

acid and/or sodium hydroxide solution, was used as a test solution.   Effluent samples, which were

obtained from a jewelry factory, were digested with hydrochloric acid on heating [28] after filtration

using a membrane filter (Nihon Millipore, Omnipore membrane, pore size of 0.45 µm).   The pH of

the sample solutions was approximately 1.   For analyses of platinum metal and its alloy,

approximately 0.1 g of a platinum metal (Pt, 99.95%) or platinum alloy (Pt, 94.82%; Cu, 5.16%)

was dissolved in 20 mL of aqua regia on heating.   The solution was then diluted with 0.1 mol L^{-1}

hydrochloric acid.

To 8 mL of the test solution or the sample solution, a mixture of 1.0 mL of acetone and

100 µL of chloroform containing 50 mmol L^{-1} of dicyclohexylamine was swiftly injected.   The

cloudy solution was gently shaken, and ultrasonic irradiation was carried out for 5 min.   The

solution was then centrifuged.

Gold in the sedimented phase was determined using ETAAS under the operating conditions summarized in **Table 1**. Solutions for the calibration curve were prepared using 8 mL of 0.1 mol L^{-1} hydrochloric acid spiked with appropriate amounts of gold(III). A blank test was also carried out using 0.1 mol L^{-1} hydrochloric acid or the purified water-based solution after the treatment with hydrochloric acid or aqua regia. To optimize the extraction conditions, gold in the supernatant phase was determined using ETAAS. The extraction percentage was evaluated in a manner similar to that used for the extraction behavior of gold(III), as mentioned above.

3. Results and Discussion

3.1 Extraction of gold(III) with some amine compounds

The extraction of gold(III) using 11 kinds of amine compounds was investigated using DLLME as well as LLE in order to select the appropriate amine compound for the extraction. Since the extraction of gold(III) with amine compounds has been carried out in the acidic region [9-12], 0.1 mol L^{-1} hydrochloric acid was used for the experiments. As a water-miscible organic solvent, acetone was chosen because it has been widely utilized as a disperser solvent for DLLME [18,19,24,25].

3.1.1 Comparison of extraction behavior of gold(III) by LLE and DLLME

The results of the extraction of gold(III) using a series of amine compounds by LLE, in which 50 mL of the test solution containing 4 mg L^{-1} of gold(III) and 1 mL of chloroform containing an amine compound were used without acetone, are shown in **Fig. 1**. For *N*-methylaniline and *N*-phenylbenzylamine [11], gold(III) was quantitatively extracted. *N*-Methyldiphenylamine gave 57% of the extraction. For the other amine compounds, however, less than 30% of gold(III) was extracted, and no extraction of gold (III) was observed for dicyclohexylamine.

The results for DLLME of gold(III) using the amine compounds are summarized in **Fig. 1**. For aromatic amines, including *N*-methylaniline and *N*-phenylbenzylamine [11], the extraction percentages decreased compared to those for LLE when a mixture of 0.9 mL of acetone and 90 μL of chloroform containing 200 mmol L^{-1} of the corresponding amine compound was added to 5 mL of the test solution. In contrast, the extraction percentages were considerably improved with the use of *N*-butyldimethylamine, benzylamine, dibenzylamine, cyclohexylamine, and dicyclohexylamine. From the results of DLLME, the extraction of gold(III) with dibenzylamine and dicyclohexylamine, which gave more than 80% of the extraction, was further investigated using 5 mL of the test solution containing a much lower concentration of gold(III) (10 μg L^{-1}). The

extraction of gold(III) was almost 100% with the use of both 50 and 200 mmol L^{-1} of

dicyclohexylamine in chloroform, whereas 50 and 200 mmol L^{-1} of dibenzylamine extracted 67%

and 88% of gold(III), respectively.   These results indicate that dicyclohexylamine is an excellent

extractant for DLLME of gold(III).   The molecular-structural characteristics, including bulkiness,

the strong basicity (pK_a = 10.4 [29]), and the high lipophilicity of dicyclohexylamine may

contribute to the effective extraction of gold(III).

3.1.2 *Role of acetone on extraction of gold(III) with dicyclohexylamine*

In DLLME, a water-miscible organic solvent is used to disperse the water-immiscible

organic solvent as an extraction solvent [18-27].   The efficient dispersion of the extraction solvent

accelerates the extraction of analytes.   In our experiments using acetone as a disperser solvent,

however, the extraction efficiency in DLLME using amine compounds was not necessarily

improved compared with that in LLE as shown in **Fig. 1**, which suggests that acetone may also have

other functions in the extraction.   The role of acetone in the extraction of gold(III) with

dicyclohexylamine was therefore examined using the LLE technique.

The effect of the stirring time on the extraction of gold(III) with dicyclohexylamine using

0-10 mL of acetone is shown in **Fig. 2**.   In the absence of acetone, gold(III) was not extracted after

stirring for 2 h; the extraction percentages retained almost 0% for at least 24 h.   In contrast, the

extractability was dramatically improved in the presence of acetone (**Fig. 2**).   When 1-10 mL of

acetone was used, the solution became cloudy just after the stirring was started.   The extraction

percentages increased as the amount of acetone added was increased.   In these cases, gold(III) was

extracted after 1 min, and the extraction percentages were almost constant when further stirring was

carried out (**Fig. 2**).   The extraction of gold(III) was also observed without dicyclohexylamine; the

extraction percentages after stirring for 1 h were 0.4% for 4 mL of acetone, 3.1% for 8 mL, and

11% for 10 mL.   On the other hand, 68% of gold(III) was extracted even when 1 mL of chloroform

containing 200 mmol L^{-1} of dicyclohexylamine was slowly added to a mixture of 50 mL of 0.1 mol

L^{-1} hydrochloric acid containing 4 mg L^{-1} of gold(III) and 10 mL of acetone and the mixture was

allowed to stand statically for 260 h, whereas the extraction of gold(III) was not observed in the

absence of acetone.   These results suggest that acetone is not merely the disperser.

It has been reported that in the extraction of some elements with aliphatic tertiary amines

[30-32], the extraction percentages were considerably improved by the addition of water-miscible

organic solvents, including methanol, ethanol, and acetone, which are generally utilized as disperser

solvents in DLLME [18-27].   Such phenomena have been attributed to the decrease in hydration as

the mole fraction of water decreased [30-32], resulting in the increased stability of negatively

charged chloro-complexes in solution [31].   The enhancement of the extraction percentage is also

discussed from the standpoint of the differences in the dielectric constants between the aqueous

phase and the organic phase [32].   The contents of water and the water-miscible organic solvent in

the organic phase as well as that of the water-miscible organic solvent in the aqueous phase

increased as the added amount of water-miscible organic solvent was increased.   The difference in

the dielectric constants between the aqueous phase and the organic phase was therefore decreased.

The decreases in hydration and in the differences in the dielectric constants resulted in the effective

extraction of some elements [32].   In the case of the gold(III) extraction with dicyclohexylamine,

acetone would play similar roles in addition to acting as a disperser solvent.

　　　When the added amount of acetone increased, the volume of the sedimented phase

increased due to the increase in the distribution of acetone and water to chloroform [32].   In our

experiment, a similar tendency was observed, but all the volumes of the sedimented phases with

various amounts of acetone were less than those of chloroform added.   These results indicate that

the supernatant phase is a homogeneous ternary solvent mixture containing water, acetone, and

chloroform; that is, acetone promotes the dissolution of chloroform into the supernatant phase.

The dissolution of chloroform to the supernatant solution and the phase separation arise reversibly,

and the separated chloroform is expected to extract gold(III) effectively.   Such an extraction,

which is inherently similar to HoLLE [13-16], would also take place in DLLME of gold(III) with

dicyclohexylamine.

　　　The relationship between the distribution ratio of gold(III) (D) and the initial

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concentration of dicyclohexylamine in chloroform ($[DCHA]_{org}$) was examined in the presence of 1-10 mL of acetone.   The D value was corrected based on the volume of the sedimented phase.   As shown in **Fig. 3**, linear relationships between log D and log $[DCHA]_{org}$ were obtained under all amounts of acetone.   The slopes for 1 mL and 2 mL of acetone were 1.05 and 0.98, respectively.   These results indicate that the dominant extracted species of gold(III) should be 1 : 1 for tetrachloroaurate(III) ion : protonated dicyclohexylamine under these conditions.   The extraction of gold(III) with dicyclohexylamine may obey the ion-pair mechanism, as it does with the other amine compounds [9-12].   However, the slope gradually decreased with an increase in the amount of acetone, which may have been caused, in part, by a dissociation of the extracted species occurring in the sedimented phase.   The variation of the dicyclohexylamine concentration in the sedimented phase and the extraction of gold(III) without dicyclohexylamine would also be possible reasons.

3.2   *Optimum conditions for DLLME of gold(III) with dicyclohexylamine*

As mentioned above, dicyclohexylamine was useful as an extractant for the DLLME of gold(III).   We optimized the conditions for DLLME of gold(III) with dicyclohexylamine using 8 mL of the test solution.

3.2.1 Water-miscible organic solvent

The influence of some water-miscible organic solvents, including acetone, acetonitrile, methanol, and acetic acid, was investigated.   As shown in **Fig. 4**, acetone was the most suitable of the investigated solvents in terms of effective extraction and ease of handling.   The extraction percentage of gold(III) increased with an increase in the amount of acetone used, whereas gold(III) was not extracted in the absence of acetone.   The quantitative extraction of gold(III) was achieved using 1.0 -1.5 mL of acetone.   Therefore, 1.0 mL of acetone was used in this method.

3.2.2 Water-immiscible organic solvent as extraction solvent

Chloroform was a convenient extraction solvent in gold(III) extraction using dicyclohexylamine because of the easy dissolution of dicyclohexylamine and the efficient extraction of gold(III).   **Figure 5** shows the effect of the volume of chloroform, which contained 50 mmol L^{-1} of dicyclohexylamine, on both the extraction of gold(III) and the volume of the sedimented phase.   The extraction percentage of gold(III) increased with an increase in the volume of chloroform and reached approximately 100% when more than 100 μL of chloroform was used.   Additionally, the volume of the sedimented phase increased with an increase in the volume of chloroform used, whereas each volume of the sedimented phase after the extraction scarcely varied.   Due to the quantitative extraction of gold(III) and the high enrichment factor, 100 μL of chloroform

was used in this method.

3.2.3 Dicyclohexylamine

When the extraction was carried out using a mixture of acetone and chloroform not containing dicyclohexylamine, $26 \pm 2.8\%$ (mean $\pm$ standard deviation, n=3) of gold(III) was extracted.   The extraction percentage increased with an increase in the concentration of dicyclohexylamine; more than 90% of gold(III) was extracted with the use of more than 30 mmol L^{-1} of dicyclohexylamine in chloroform.   In this method, 50 mmol L^{-1} of dicyclohexylamine was used.

3.2.4 Extraction time

When a mixture of 1.0 mL of acetone and 100 µL of chloroform containing 50 mmol L^{-1} dicyclohexylamine was injected, the extraction percentage of gold(III) was $66 \pm 7.1\%$ (n=3) without shaking due to the insufficient dispersibility of chloroform [19].   However, the extraction percentage of gold(III) was significantly improved to $95 \pm 1.6\%$ (n=3) when the mixture was gently shaken by hand for a few seconds.   In this method, ultrasonic irradiation was applied after the gentle shaking for just in case.   Since the irradiation time, ranging from 1 to 30 min, did not affect the extraction percentages, ultrasonic irradiation for 5 min was employed.   It may be possible to

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omit the ultrasonic irradiation, depending on the sample.

3.2.5 Extraction pH

The relationship between the extraction percentage of gold(III) and the pH or acidity of the test solution is shown in **Fig. 6**. In the initial pH range of 1-3, gold(III) was quantitatively extracted. The extraction percentage of gold(III) decreased with an increase in the concentration of hydrochloric acid in the range of 1-3 mol L^{-1}, which might be due to the formation of tetrachloroauric acid (HAuCl$_4$) and/or interference by chloride ions. On the other hand, the extraction percentage also decreased with an increase in the initial pH in the range of 3-7. In this range, the pH in the supernatant phase was significantly shifted to the basic region after the extraction, whereas the pH shift was slight or negligible at an initial pH below 3. The insufficient extraction at an initial pH above 3 would be due to a lack of the protonated form of dicyclohexylamine as well as the ligand displacement of tetrachloroaurate(III) ion in the test solution. In this method, the extraction was carried out using a sample solution adjusted to pH 1.

3.2.6 Selectivity

The extraction of other elements, including iron(III), cobalt(II), nickel(II), copper(II), palladium(II), and platinum(IV), was also investigated at an initial pH range of 1-3 and an acid

concentration range of 1-3 mol L^{-1}.   Iron(III), cobalt(II), nickel(II), and copper(II) were scarcely extracted under the conditions used for the investigation (the obtained results are shown in **Fig. 2S** in the Supplementary Material).   For palladium(II), the extraction was negligible at an initial pH below 1, whereas the formation of the precipitate was observed at an initial pH above 3 (**Fig. 2S**). Although the extraction percentage of platinum(IV) slightly increased with an increase in acidity in the test solution, platinum(IV) was not extracted at an initial pH of 1-3 (**Fig. 2S**).   These results indicate that DLLME using dicyclohexylamine is quite selective for gold(III).   It is known that the extractability of gold(III) is higher than those of palladium(II) and platinum(IV) in the ion-pair extraction of their chloro-complexes [33].   In our experiments, the selectivity might have been emphasized by the use of small amounts of dicyclohexylamine.

3.3   Calibration curve and detection limit

The relationship between the absorbance of gold in the ETAAS measurement and the concentration of gold(III) was investigated.   A straight line ($R^2 = 0.996$) was obtained with the use of 8 mL of the test solution containing 0.02-1.0 $\mu g\ L^{-1}$ of gold(III).   The enrichment factor, which was calculated based on the slopes for the calibration curves with or without the extraction [25], was 60.   The detection limit, defined as three times the standard deviation for the procedural blank (n=8), was 0.002 $\mu g\ L^{-1}$ of gold(III) in 8 mL of sample solution; this value was slightly lower than

the detection limit in the combined method with DLLME and ETAAS reported previously [25].

3.4 Interference

The effect of ions generally contained in various water samples on the extraction of

gold(III) was investigated.   The concentration of the ions ($1.1×10^7$ µg L^{-1} of sodium, $4.1×10^5$ µg

L^{-1} of potassium, $1.3×10^6$ µg L^{-1} of magnesium, $4.2×10^5$ µg L^{-1} of calcium, $1.6×10^6$ µg L^{-1} of

phosphate, and $2.8×10^6$ µg L^{-1} of sulfate) in the test solution used for the investigation was nearly

equal to that in seawater [1].   More than 87% of gold(III) was extracted in the presence of large

amounts of these ions (**Table 1S** in the Supplementary Material).   The obtained results indicate

that the method proposed here is useful for determining gold(III) in various water samples,

including effluents.

The effect of excessive amounts of platinum(IV) and copper(II), which were scarcely

extracted at an initial pH of 1 (**Fig. 2S**), was also investigated.   Gold(III) was extracted at more

than 92% in the presence of 2000 µg L^{-1} of platinum(IV) and copper(II) (**Table 2S** in the

Supplementary Material).   These results indicate that the proposed method is also applicable to the

determination of gold as an impurity in platinum metal and alloys containing platinum and copper.

3.5 Application

The method proposed here was applied to the determination of gold(III) in effluents. The obtained results are shown in **Table 2**.   In all of the effluent samples, gold(III) was precisely determined.   The gold(III) spiked to the effluent samples was quantitatively recovered, and no significant interference was observed.

The determination of gold in platinum metal and its alloy was also attempted.   As shown in **Table 3**, gold was determined in both samples, and satisfactory results were obtained in the recovery tests.

4.   Conclusion

Dicyclohexylamine as an extractant for gold(III) showed excellent performance in DLLME using acetone as a disperser solvent and chloroform as an extraction solvent.   The results of the investigation using the LLE technique suggest that acetone used as a disperser solvent in DLLME also contributes to decrease in hydration, decrease in the difference in the dielectric constants between the supernatant phase and the sedimented phase, and dissolution of a part of chloroform as an extraction solvent to the supernatant phase.   The extraction of gold(III) in DLLME using dicyclohexylamine is, therefore, quite efficient.   Gold(III) can be selectively extracted from a sample solution at pH 1 even in the presence of other elements, such as iron(III),

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cobalt(II), nickel(II), copper(II), palladium(II), and platinum(IV). The combined method with

DLLME and ETAAS can readily determine gold(III) at a sub-μg L^{-1} level using only 8 mL of the

sample solution without interference by the matrices and can be applied to the determination of gold

in platinum metal and its alloy as well as effluent.   The proposed method should be useful for the

analyses of other water samples and the determination of gold in various materials, including metals,

alloys, and salts.

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Table 1 Operating conditions for FAAS and ETAAS

Analytical wavelength (nm)	242.8
Lamp current (mA)	10
Slit width (nm)	1.3
< FAAS >	
Flame conditions	
Air pressure (kPa)	160
Acetylene pressure (kPa)	20
< ETAAS >	
Cuvette	Pyro-coated graphite tube
Carrier gas (Ar) flow rate (mL min^{-1})	200
Injection volume (μL)	10
Atomizer program	
Dry (ºC, s)	80-120, 30
Ash (ºC, s)	400, 30
Atomize (ºC, s)	2700, 7
Clean (ºC, s)	2800, 3

Table 2   Results for determination of gold(III) in effluent

Sample [a]	Au added (ng in 8 mL)	Au found [b] (ng in 8 mL)	Au concentration ($\mu g\ L^{-1}$)	Au recovery (%)
Effluent 1 [c]	-	2.3 ± 0.14	5.7	
	0.8	3.0 ± 0.06		98
Effluent 2 [c]	-	1.4 ± 0.07	3.4	
	0.8	2.1 ± 0.07		96
Effluent 3	-	2.9 ± 0.12	0.36	
	0.8	3.7 ± 0.08		103

a. Effluents were sampled at different time in the same day.

b. Mean ± standard deviation (n=3).

c. Effluent was diluted to 20 times with 0.1 mol L^{-1} hydrochloric acid after the digestion.

Table 3 Results for determination of gold in platinum metal and platinum alloy

Sample	Au added (ng in 8 mL)	Au found [a] (ng in 8 mL)	Au content ($\mu g\ g^{-1}$)	Au recovery (%)
Pt metal	-	0.76 ± 0.03	$39._9$	
	0.8	$1.5_8 \pm 0.03$		104
Pt alloy	-	0.57 ± 0.02	$28._1$	
	0.8	$1.3_6 \pm 0.02$		99

a. Mean ± standard deviation (n=3).

Figure captions

Fig. 1   Extraction of gold(III) with 11 kinds of amine compounds using normal LLE and DLLME

techniques.

Aqueous phase, 0.1 mol L^{-1} HCl containing 4 mg L^{-1} of Au(III); organic phase, chloroform

containing 200 mmol L^{-1} of amine compound.

LLE: 50 mL of aqueous phase and 1 mL of organic phase was stirred for 1 h.

DLLME: 1 mL of the mixture of 0.90 mL of acetone and 90 µL of organic phase was injected

swiftly to 5 mL of aqueous phase, and the cloudy solution was gently shaking for 10 s.

Fig. 2   Extraction percentage of gold(III) as a function of stirring time on LLE.

Aqueous phase, 50 mL of 0.1 mol L^{-1} HCl containing 4 mg L^{-1} of Au(III); organic phase, 1 mL of

chloroform containing 200 mmol L^{-1} of amine compound.   Acetone, 10 mL (◆), 8 mL (◇), 1 mL

(○), or not added (▲).

Fig. 3   Relationship between the distribution ratio of gold(III) (D) and the initial concentration of

dicyclohexylamine in chloroform ($[DCHA]_{org}$) on LLE using various amounts of acetone.

Aqueous phase, 50 mL of 0.1 mol L^{-1} HCl containing 4 mg L^{-1} of Au(III); organic phase, 1 mL of

chloroform containing 200 mmol L^{-1} of amine compound.   Acetone, 10 mL (◆), 8 mL (◇), 4 mL

(■), 3 mL (□), 2 mL (●), 1 mL (○).

Fig. 4   Effect of some disperser solvents on DLLME of gold(III) with dicyclohexylamine.

Aqueous phase, 8 mL of 0.1 mol L^{-1} HCl containing 10 μg L^{-1} of Au(III); mixture solution, 1.0 mL

of disperser solvent and 100 μL of chloroform containing 50 mmol L^{-1} of dicyclohexylamine;

shaking, 10 s; ultrasonic irradiation, 5 min.

The results were shown at mean ± standard deviation (n=3).

Fig. 5   Effect of volume of chloroform on DLLME of gold(III) with dicyclohexylamine.

Aqueous phase, 8 mL of 0.1 mol L^{-1} HCl containing 10 μg L^{-1} of Au(III); mixture solution, 1.0 mL

of acetone and 50-250 μL of chloroform containing 50 mmol L^{-1} of dicyclohexylamine; shaking, 10

s; ultrasonic irradiation, 5 min.

The results were shown at mean ± standard deviation (n=3).

Fig. 6   Effect of HCl concentration and pH on DLLME of gold(III) with dicyclohexylamine.

Aqueous phase, 8 mL of 0.1 mol L^{-1} HCl containing 10 μg L^{-1} of Au(III); mixture solution, 1.0 mL

of disperser solvent and 100 μL of chloroform containing 50 mmol L^{-1} of dicyclohexylamine;

shaking, 10 s; ultrasonic irradiation, 5 min.

The extraction percentage was plotted as a function of the initial (◆) or final (◇) pH.
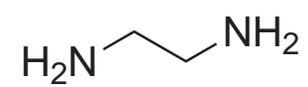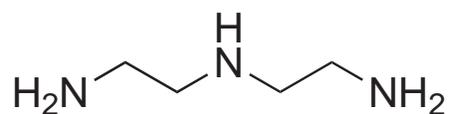
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Diethylenetriamine
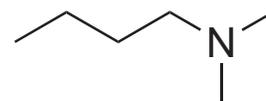
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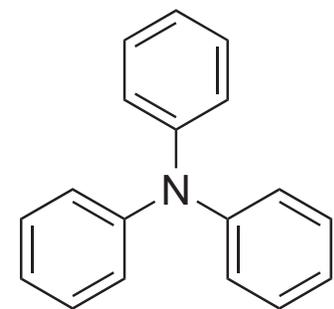
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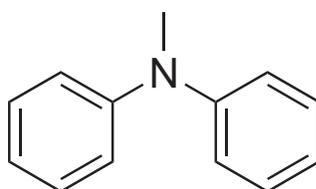
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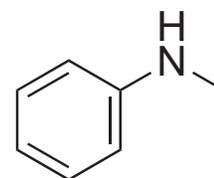
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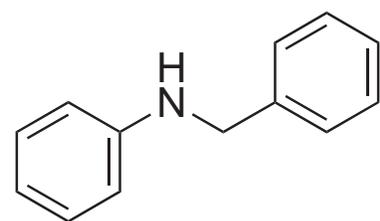
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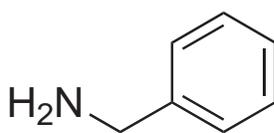
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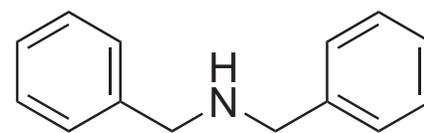
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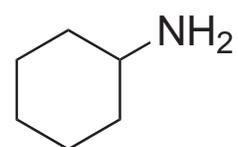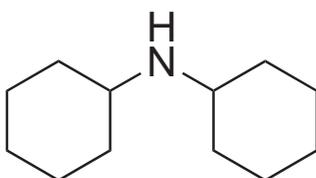
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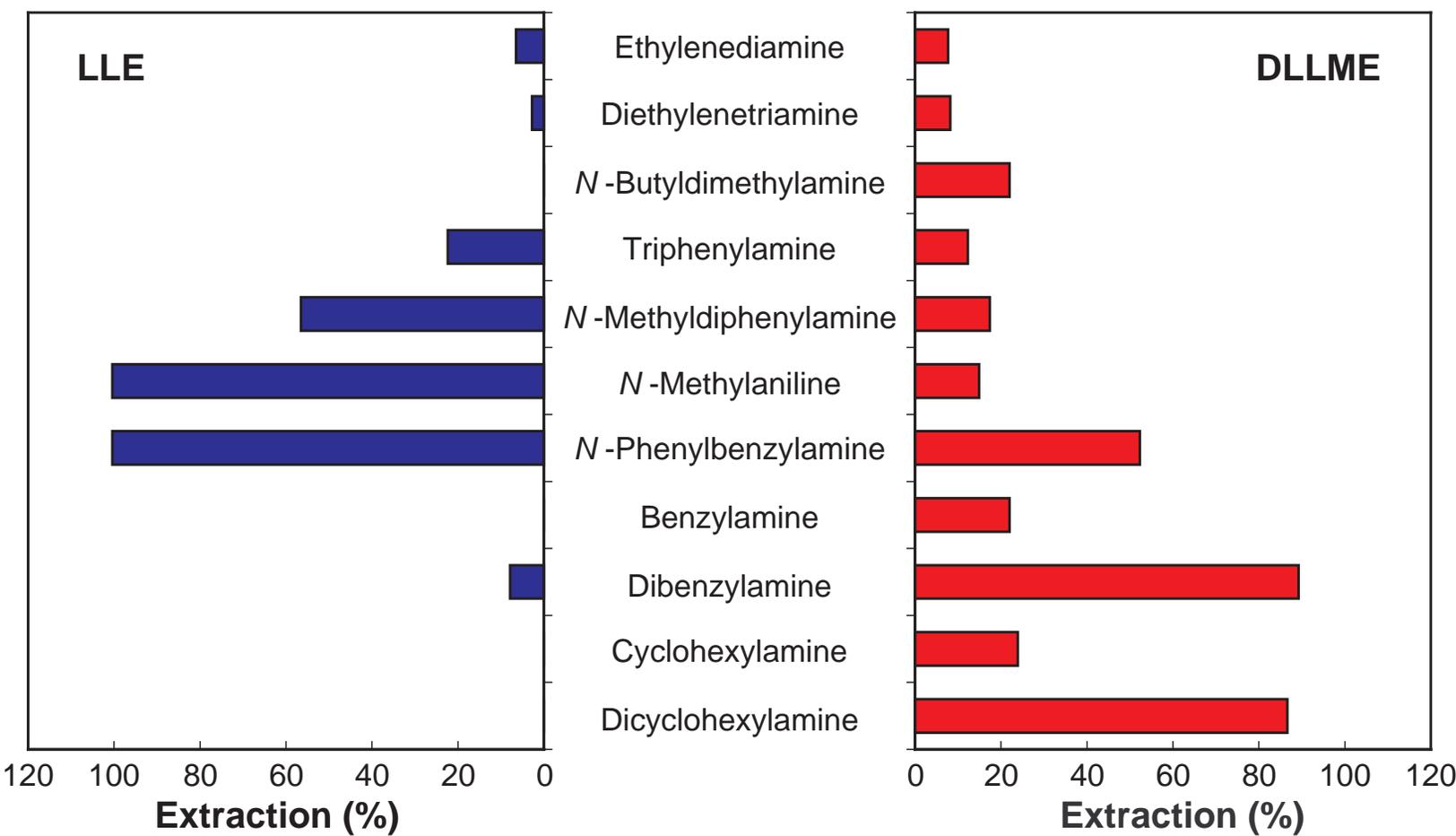
Fig. 1 S. Kagaya, et al
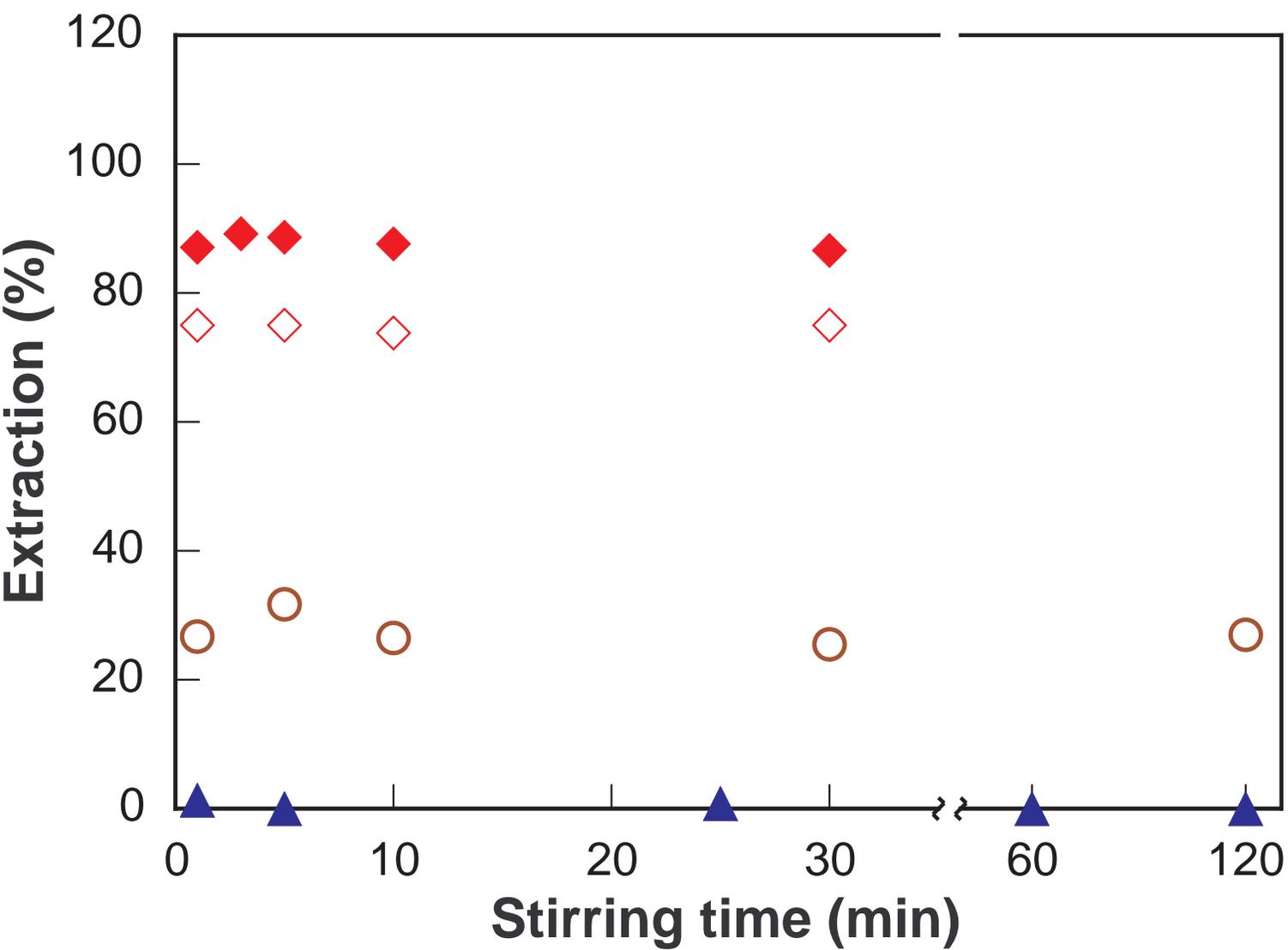
Fig. 2 S. Kagaya, et al

Fig. 3 S. Kagaya, et al
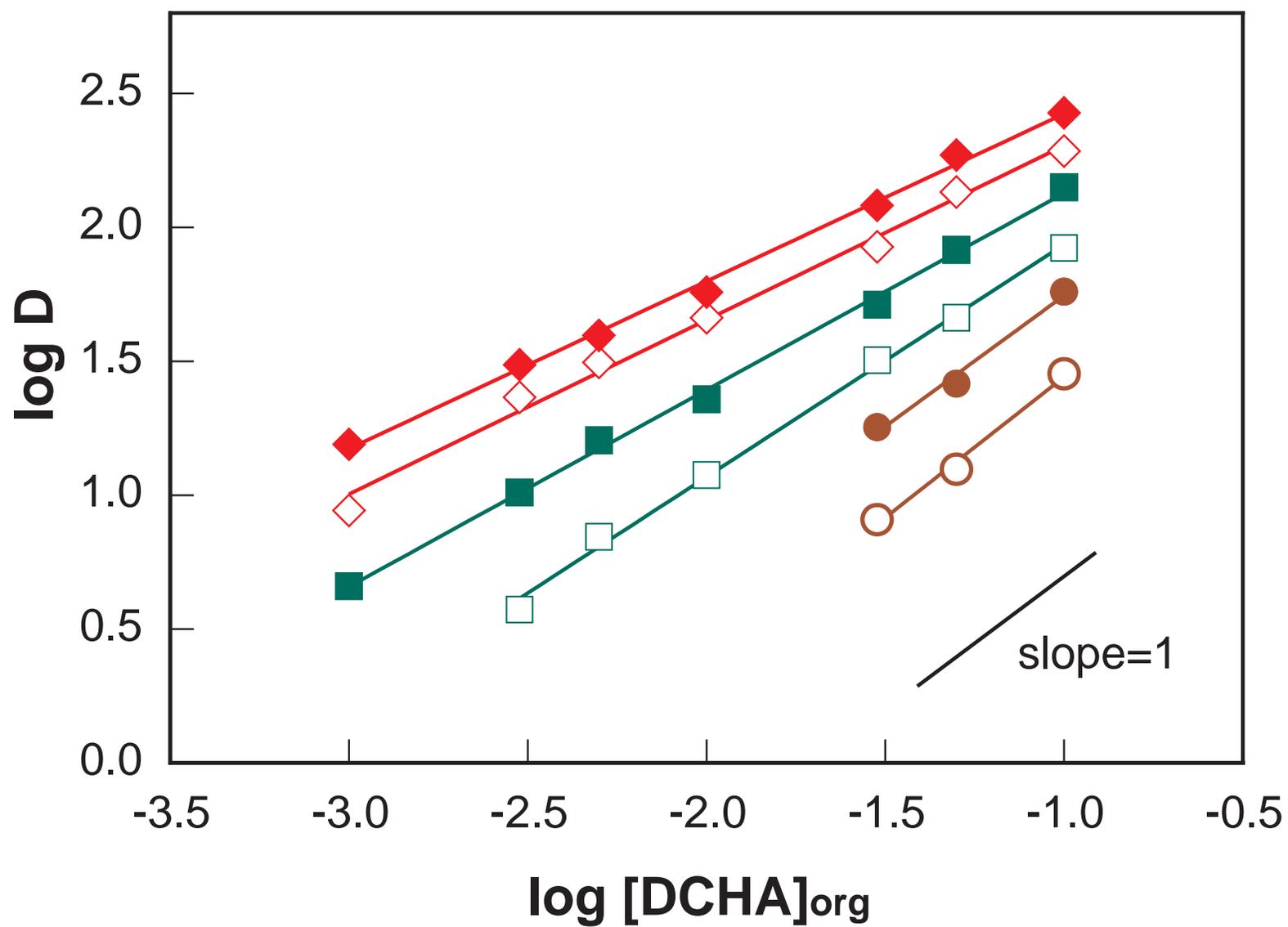
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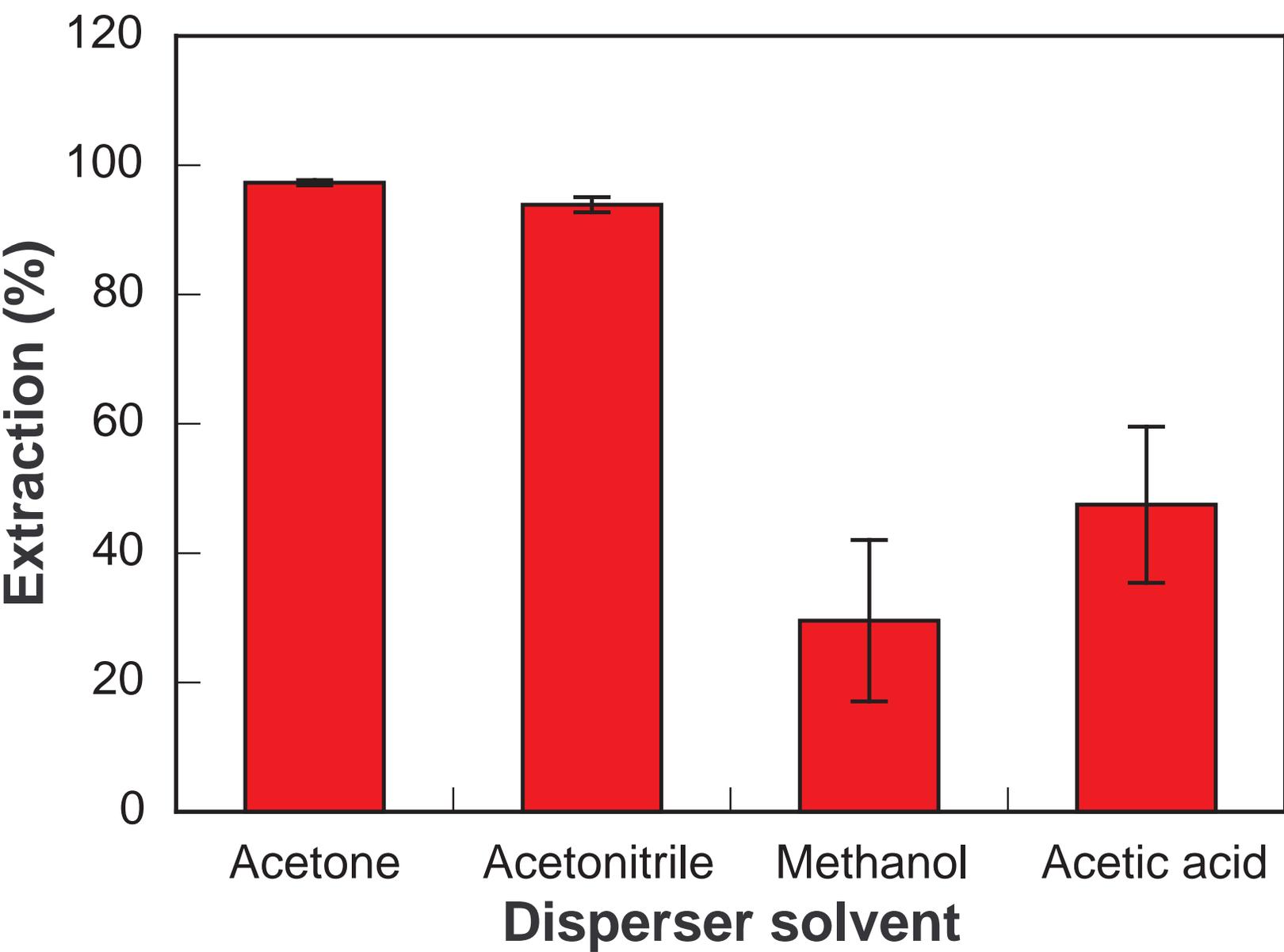
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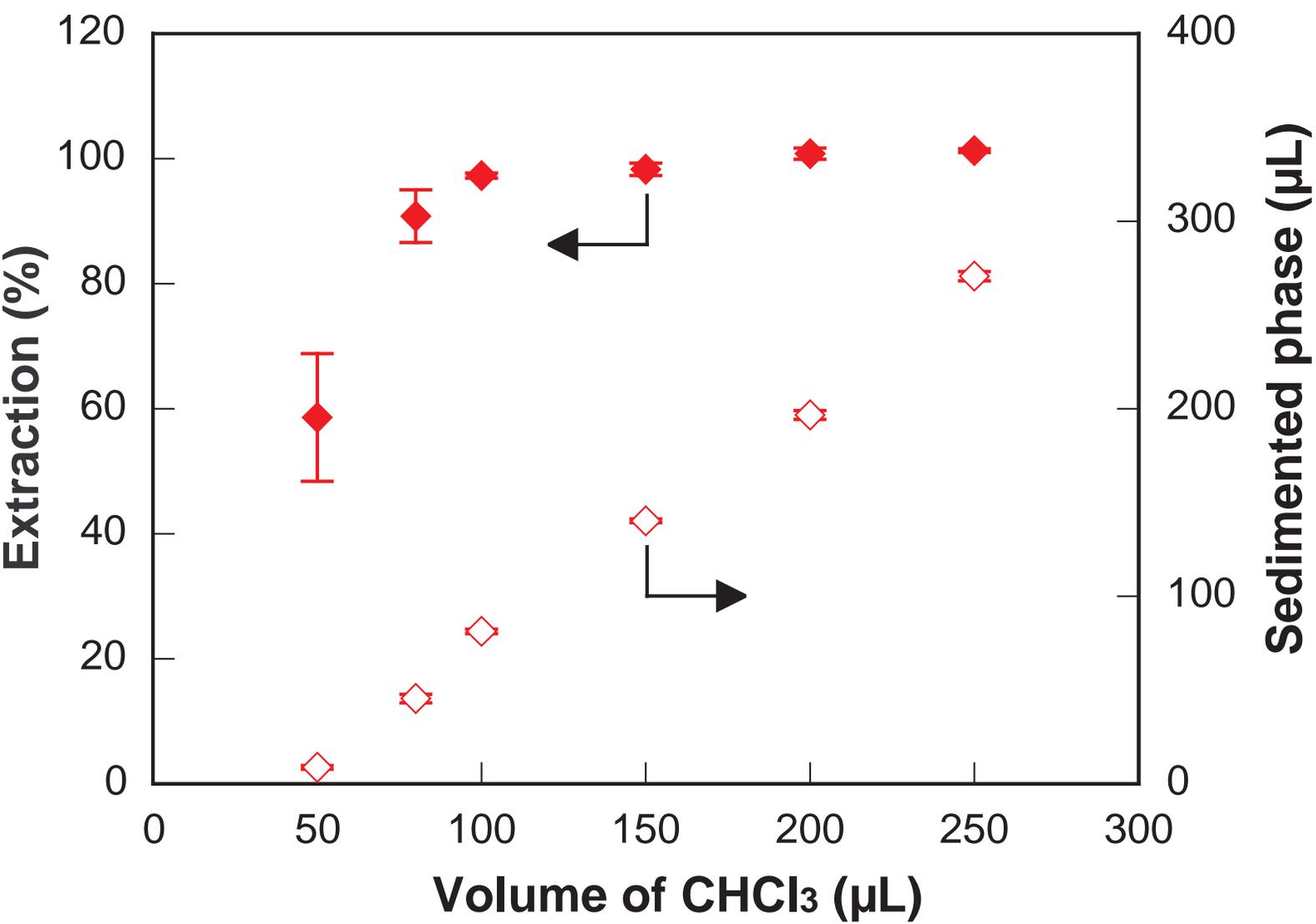
Fig. 6 S. Kagaya, et al

Fig. 7 S. Kagaya, et al