Solidified Floating Organic Drop Microextraction for Speciation of Inorganic As and Sb and Their Determination by Electrothermal Vaporization ICP-MS

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INTRODUCTION

It is well known that arsenic (As) and antimony (Sb) are ubiquitous elements in the environment due to their wide application in the production of pharmaceuticals, alloys, glasses, infrared detectors, diodes and semiconductors. It is known to be one of the most toxic elements and has serious effects on plants, animals and human health (1, 2). Sb, as a cumulative toxic element, has toxicological properties similar to those of As (3, 4). What is more, the toxicity, bioavailability and reactivity of As and Sb are strongly dependent on their chemical forms (5-8). The inorganic species of As and Sb are more toxic than their organic forms (9, 10). The toxicity of As(III) and Sb(III) is 10-20 times higher than that of As(V) and Sb(V) (11, 12). In addition, their oxides have shown to cause several types of cancer (13). In the majority of environmental samples such as natural water and fly ash, As and Sb are usually present as As(V)/As(III) and Sb(V)/Sb(III), because these oxidation states are the most environmentally mobile and geochemically important forms of these elements (14, 15). Hence, simple, fast, sensitive, reproducible and accurate analytical methods for the speciation of inorganic As and Sb in natural water are required for evaluating their possible effect on fauna, flora, and human health.

In general, elemental speciation can be carried out by combining a

ABSTRACT

Based on solidified floating organic drop microextraction (SFODME), a novel method was developed for the simultaneous speciation of inorganic arsenic (As(V)/As(III)) and antimony (Sb(V)/Sb(III)) by electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS). Ammonium pyrroline-dithiocarbamate (APDC) was used as both a chelating reagent in SFODME and a chemical modifier in ETV. As(III)/Sb(III) could react with APDC to form complexes at pH 5.5, and the complexes were quantitatively extracted into organic phase of 1-dodecanol, whereas As(V)/Sb(V) remained as free species in the aqueous phase. As(III)/Sb(III) was directly determined by ETV-ICP-MS. Total As/Sb was determined by the same method after reducing As(V)/Sb(V) to As(III)/Sb(III). The assay of As(V)/Sb(V) was obtained by subtracting As(III)/Sb(III) from total As/Sb. The main factors affecting the separation and determination, including pH, amount of APDC, extraction time, stirring rate, sample solution volume and temperature program, were examined in detail. Under the optimized conditions, the detection limits were 0.18 pg mL^{-1} for As(III) and 0.37 pg mL^{-1} for Sb(III). The relative standard deviations for As(III) and Sb(III) were 4.7% and 5.9% ($c=1.0 \text{ ng mL}^{-1}$, $n=9$), respectively. This method was applied for the simultaneous speciation of inorganic arsenic and antimony in natural water samples and standard reference materials with satisfactory results.

sensitive detection technique with an effective separation method. Although the combination of chromatography with a specific element detector is a powerful tool for speciation, non-chromatographic methodology is still an attractive alternative because it can offer simple and inexpensive ways for the discrimination of specific or toxic forms of an element (16, 17). Many non-chromatographic techniques such as coprecipitation, solvent extraction, cloud point extraction, solid phase extraction, ion exchange, hydride generation and liquid phase microextraction (LPME) have been used for elemental speciation (18-24). It is worth noting that recently a new LPME technique, namely solidified floating organic drop microextraction (SFODME), has drawn considerable attention in analytical chemistry. Owing to its unique merits of simplicity, speed, low cost, consumption of small amounts of organic solvent and high enrichment factor, SFODME has been widely used for the analysis of trace elements (25). However, to the best of our knowledge, the use of SFODME for the simultaneous speciation of inorganic As and Sb has not been reported in the literature.

At present, atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS) still represent the most important routine techniques for elemental analysis (26-35). However, AAS greatly suffers from limited matrix tolerance and single-element detection ability in

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real sample analysis. ICP-AES allows fast and multielement analysis, but it often suffers from line-rich spectrum interferences of some elements. Relatively, ICP-MS is the most favorable choice for elemental analysis owing to its high sensitivity, wide linear range, and rapid multielement detection capability without encountering line-rich spectrum interferences in ICP-AES. It is predicted that SFODME coupled with ICP-MS may be a powerful detection tool for elements. Unfortunately, the solution nebulization sample introduction procedure used for conventional ICP-MS is not compatible with SFODME because of its large sample consumption. In addition, organic solvents used in SFODME may lead to destabilization or extinction of the ICP discharge owing to the relatively high solvent vapor pressure and solvent loading (36). Thus, the development of a suitable sample introduction technique with a small amount of sample consumption and *in situ* removal of the organic solvent is a promising and prospective work for extending the application of the SFODME technique.

In comparison to solution nebulization, electrothermal vaporization (ETV) as a sample introduction device with ICP-MS has the benefit of high introduction efficiency, small sample requirement, and low absolute detection limits. Moreover, use of a chemical modifier in ETV could greatly improve the analytical performance of the method (37). As described previously, SFODME is a miniaturized sample pretreatment technique, and ETV consists of a microamount sample introduction device. Therefore, SFODME coupled with ETV for ICP-MS may be a perfect combination. However, most work has been done using SFODME coupled with AAS for the separation and preconcentration of trace elements (38-42) and only few studies reported using ICP-MS (43, 44). It is especially

worth noting that use of SFODME-ETV-ICP-MS for elemental speciation has so far received little attention.

In the present work, an attempt was made to develop SFODME coupled with ETV-ICP-MS for the simultaneous speciation of inorganic arsenic and antimony. Ammonium pyrroinedithiocarbamate (APDC) was used as both a chelating reagent in SFODME and a chemical modifier in ETV for the separation, preconcentration, and volatilization of As(III), As(V), Sb(III), and Sb(V) prior to their determination by ICP-MS. The main factors affecting the determination of the analytes were investigated in detail. The feasibility of this method was assessed by its application for the simultaneous speciation of inorganic As and Sb in natural water samples and standard reference materials.

EXPERIMENTAL

Instrumentation

An X-7 ICP-MS system (Thermo Fisher Scientific, USA), equipped with a modified commercially available WF-4C graphite furnace (Beijing Second Optics, P.R. China) as an electrothermal vaporizer, was used for the determination of the analytes. The operating parameters of the ICP-MS were optimized with a concentric glass nebulizer prior to connection with the ETV device. A pyrolytic graphite tube was used throughout this work. The working conditions of ETV-ICP-MS are summarized in Table I. The pH value of the solution was controlled with a pH meter (Thermo Fisher Scientific, USA) supplied with a combined electrode.

TABLE I
Operating Parameters for ETV-ICP-MS

ICP-MS Plasma	
Plasma power	1300 W
Plasma argon flow rate	14.5 L min ⁻¹
Auxiliary argon flow rate	0.85 L min ⁻¹
Nebulizer argon flow rate	0.92 L min ⁻¹
Sampler orifice (nickel)	1.1 mm
Skimmer orifice (nickel)	0.7 mm
Acquisition mode	Peak jumping
Number of sweeps	100
Dwell time	10 ms
Acquisition time	40 s
Number of measurements per peak	3
Isotopes	⁷⁵ As, ¹²¹ Sb
ETV	
Sample volume	10 µL
Carrier gas flow rate	0.45 L min ⁻¹
Drying step	100 °C, ramp 10 s, hold 10 s
Ashing step	200 °C, ramp 10 s, hold 30 s
Vaporization step	2000 °C, hold 4 s
Clear-out temperature	2600 °C

Standard Solutions and Reagents

Unless otherwise stated, all reagents used in this study were of high purity or at least of analytical grade. High purity deionized water obtained from a Milli-Q® A10 system (Millipore Corporation, USA) was used throughout this work.

The stock standard solutions (1.0 mg mL⁻¹) of As(III), As(V), and Sb(III) were obtained by dissolving appropriate amounts of Na₃AsO₃, Na₃AsO₄, and K(SbO)C₄H₄O₆ (Tianjin Reagent Factory, P.R. China) in high purity deionized water, respectively. The stock standard solution (1.0 mg mL⁻¹) of Sb(V) was prepared by dissolving appropriate amounts of K₂H₂Sb₂O₇ (Shanghai Reagent Factory, P.R. China) in boiling water. The working solutions were prepared daily by appropriate dilution of the stock solutions. The APDC solution was prepared by dissolving a proper amount of APDC (Shanghai Reagent Factory, P.R. China) in 1-undecanol (Shanghai Reagent Factory, P.R. China). Monomethylarsonic acid, dimethylarsinic acid and trimethyl antimony bromide were obtained from Sigma-Aldrich (Germany). All glass and polypropylene ware was kept in 2.0 mol L⁻¹ HNO₃ solution for at least one night, then rinsed with 0.1 mol L⁻¹ HNO₃ solution, and before use with twice-distilled water.

Sample Preparation

Water samples of river water (Yangtze River, Wuhan, P.R. China) and lake water (Dongxi Lake, Wuhan, P.R. China) were collected in 50-mL polyethylene containers, respectively. All water samples were filtered through a 0.45 μm membrane filter, then stored in polyethylene bottles at 4 °C for future use. The storage period was kept as short as possible. Blanks were prepared exactly as the samples, except no addition of analytes.

SFODME Extraction

In this work, the SFODME device used for the extraction of the analytes was similar to that as described in the literature (45). The sample solution containing the analytes was adjusted to pH 5.5 using diluted nitric acid or ammonium hydroxide. Then 10 mL of the resulting solution was transferred into an 11-mL vial, and a stir bar and 20 μL of APDC in 1-dodecanol were added. The magnetic stirrer was turned on, and the solution was stirred for a fixed time. In this step, the analytes reacted with APDC to form hydrophobic complexes and were extracted into 1-undecanol. After the extraction process was finished, the sample vial was transferred into an ice bath until the organic solvent solidified. The solidified solvent was then transferred into a conical vial where it immediately melted at room temperature. The extract was diluted to 100 μL with tetrahydrofuran (THF). Finally, 10 μL of the extract was injected into the ETV for ICP-MS analysis.

ETV-ICP-MS Procedure

After the ETV unit was connected to the ICP-MS, 10 μL of the analytes in the organic solvent was injected into the graphite furnace. During the drying and charring process, the dosing hole of the graphite furnace was kept open to remove the water and the organic vapor. Then it was sealed with a graphite probe for 5-10 seconds prior to the vaporization step, the vaporized analytes were swept into the plasma excitation source by a carrier gas, and the peak-hop transient mode for data acquisition was used for the detection of the analytes.

Data Analysis

In order to accurately calculate the concentration of the analytes, the effects of common organic forms of As and Sb in natural water

samples on the extraction and determination of the analytes was investigated in this work, including monomethylarsonic acid, dimethylarsinic acid, and trimethylantimony (46, 47). The results showed that they did not affect the extraction and determination of the analytes under the selected conditions. Thus, the extracted analytes diluted with THF were introduced into the ETV-ICP-MS for the direct determination of As(III) and Sb(III).

The concentration of As(V)/Sb(V) was calculated by their respective differences between total As/Sb and As(III)/Sb(III) concentration. Total As/Sb was determined after the reduction of As(V)/Sb(V) to As(III)/Sb(III). Prereduction of As(V)/Sb(V) to As(III)/Sb(III) was carried out with 0.5% (w/v) L-cysteine media for 30 minutes in a boiling water bath (53).

RESULTS AND DISCUSSION

Signal Profiles of As(III) and Sb(III)

Figure 1 shows the typical signal profiles of As(III) and Sb(III) with and without the addition of APDC as a chemical modifier. It can be seen from Figure 1 that in the absence of APDC, As(III) (b) and Sb(III) (b') were partly vaporized at 2000 °C, and their severe memory signals were recorded (c and c'). In the presence of APDC, however, the intensive signals of As(III) (d) and Sb(III) (d') were detected at the same vaporization temperature, and no memory signals were observed for As(III) and Sb(III) even at 2600 °C (e and e'). In addition, their blank signals were not found in this experiment (a and a'). The possible reason for this is that As(III) and Sb(III) can form thermally stable and volatile As(III)-APDC/Sb(III)-APDC complexes. Thus, APDC was selected as the suitable chemical modifier for ETV-ICP-MS.

Effect of pH on SFODME

It is well known that the pH of the sample solution plays an essential role in complex formation and subsequent extraction. Thus, the effects of pH on the signal intensity of As(III), As(V), Sb(III), and Sb(V) were investigated in the pH range of 1.0-7.0. As shown in Figure 2, maximal signal intensity of As(III) and Sb(III) was obtained in the pH range of 2.0-6.5, whereas the signal intensity of As(V) and Sb(V) was hardly detected in the pH range of 5.0-6.5. The reason for this is that As(III) and Sb(III) can react with APDC to form 1-dodecanol extractable As(III)-APDC/Sb(III)-APDC complexes, but As(V) and Sb(V) do

not form APDC complexes extracted by 1-dodecanol. Based on the results mentioned above, a pH of 5.5 was used for the separation of the different species of inorganic As and Sb.

Quantitative Vaporization of Analytes

In this work, the quantitative vaporization of As(III), As(V), Sb(III) and Sb(V) was investigated with the addition of APDC at pH 5.5. The results in Figure 3 show that the signals for As(V) (f)/Sb(V) (f') can hardly be detected with APDC. In the presence of APDC, however, the intense and symmetrical signals for total As (g)/Sb (g')

were recorded due to the formation of the As(III)-APDC/Sb(III)-APDC complex. It is worth noting that the signal intensity of total As (g)/Sb (g') is about 50% of that for total As (h)/Sb (h') after the reduction by L-cysteine. The reason for this is that both As(V)/Sb(V) were reduced into As(III)/Sb(III) to result in the increase of their concentration. In addition, blank signals were not observed in the experiment (i and i'). These facts indicate that the analytes can be quantitatively vaporized and transported from the ETV to the ICP under the selected conditions.

Effect of APDC Concentration

The effect of APDC concentration on the signal intensity of the analytes was studied in the concentration range of 0.1×10^{-2} - 4.0×10^{-2} mol L⁻¹. The results in Figure 4 indicate that the signal intensity of As(III)/Sb(III) was increased with an increase in the APDC concentration from 0.1×10^{-2} to 1.0×10^{-2} mol L⁻¹, and then kept nearly constant when the concentration of the APDC exceeds 2.0×10^{-2} mol L⁻¹. Thus, the concentration of 3.0×10^{-2} mol L⁻¹ APDC was used in subsequent work.

Influence of Extraction Time

In order to achieve good precision, sensitivity, and speed, it is necessary to select an extraction time that guarantees the achievement of equilibrium between the aqueous and organic phase, and maximizes extraction efficiency. For this reason, the effect of extraction time on the signal intensity of As(III)/Sb(III) was investigated by varying the extraction time between 10 to 60 minutes. The experimental results show that the signal intensity of As(III)/Sb(III) increased with an increase in the extraction time, and then reached a plateau after 30 minutes. Thus, an extraction time of 30 minutes was used in this work.

Fig. 1. Signal profiles of As(III) and Sb(III). a and a': APDC in 1-undecanol and THF; b and b': As(III) and Sb(III) aqueous solution; c and c': residual signal from b and b' at 2600 °C; d and d': As(III) and Sb(III) with APDC in 1-undecanol and THF; e and e': residual signal from d and d' at 2600 °C. Conditions: As(III) and Sb(III) (b and b'): 20 ng mL⁻¹; As(III) and Sb(III) (d and d'): 1.0 ng mL⁻¹; vaporization temperature: 2000 °C; pH: 5.5.

Fig. 2. Effect of pH on signal intensity. Conditions: As(III)/As(V) and Sb(III)/Sb(V): 1.0 ng mL⁻¹; vaporization temperature: 2000 °C.

Influence of Stirring Rate

Agitation of the sample solution is another factor that plays an important role in enhancing the extraction efficiency and reducing the extraction time. In order to accelerate the mass-transfer of the analytes from the aqueous phase to the organic phase, the sample solution of 20 mL was continuously agitated at different stirring rates from 100 to 1200 rpm. The experimental results show that the signal intensities of the analytes increased rapidly by increasing the stirring rate up to 900 rpm. However, the signal intensity decreased obviously when the stirring rate exceeded 1000 rpm owing to the loss of float-

ing solvent drop. Hence, a stirring rate of 900 rpm was employed for further analysis.

Effect of Sample Volume

The sample volume may influence the extraction efficiency of the analytes at a given time. In addition, an increase in volume ratio of the aqueous phase to the organic phase can result in a significant increase of the enrichment factor. In order to study the effect of sample volume on extraction efficiency, some experiments were carried out using different sample volumes (5.0-40 mL). The obtained results indicate that the extraction was quantitative (recovery >90%) with

an aqueous phase volume in the range of 10-20 mL. However, a decrease was observed with a further increase in the sample volume. Based on the organic phase volume (20 μ L) and the maximum sample volume (20 mL), an enrichment factor of 1000 was obtained for the analytes. Considering the two factors of analysis time and enrichment, the sample volume of 10 mL was used for further experiments.

Effect of Interfering Ions

In order to evaluate the application potential of this method, the effects of various cations and anions commonly existing in natural water on the extraction and determination of the analytes were examined. The tolerance limit of coexisting ions is defined as the largest amount making the variation of less than 10% in the recovery of the analytes. The results show that 1000 mg L⁻¹ Cl⁻, NO₃⁻, and SO₄²⁻, 800 mg L⁻¹ K⁺ and Na⁺, 400 mg L⁻¹ Ca²⁺ and Mg²⁺, 1.0 mg L⁻¹ Al³⁺ and Fe³⁺ had no significant effect on the extraction and determination of the analytes. Thus, this method may be applied for the inorganic speciation of As and Sb in natural water samples.

Optimization of ETV Conditions

In this work, a drying temperature of 100 °C and a drying time of 10 seconds were used for removal of the water vapor. To remove the extraction solvent from the furnace as much as possible and to avoid the signal loss of the analytes at the same time, the effect of pyrolysis temperature on signal intensity was studied in the range of 100-400 °C with a pyrolysis time fixed at 20 seconds. The experimental results show that the signal intensity of As(III)/Sb(III) decreased obviously with an increase in pyrolysis temperature higher than 250 °C due to the thermal decomposition of their complexes. Based on the above facts, a pyrolysis temperature of

Fig. 3. Quantitative vaporization of analytes. *f* and *f'*: As(V) and Sb(V) with APDC in 1-undecanol and THF; *g* and *g'*: total As and total Sb with APDC in 1-undecanol and THF; *h* and *h'*: total As and total Sb with APDC in 1-undecanol and THF after reduction by L-cysteine; *i* and *i'*: APDC+L-cysteine in 1-undecanol and THF. Total As: As(III) + As(V); total Sb: Sb(III) + Sb(V); As(III), As(V), Sb(III) and Sb(V): 1.0 ng mL⁻¹; vaporization temperature: 2000 °C; pH: 5.5.

Fig. 4. Effect of APDC concentration on SFODME. As(III)/Sb(III): 1.0 ng mL⁻¹; vaporization temperature: 2000 °C; pH: 5.5.

TABLE II
Comparison of Performance Reported in Literature with Present Method

Methods	EF	DL (pg mL ⁻¹)				RSD(%)				Ref.
		As(III)	As(V)	Sb(III)	Sb(V)	As(III)	As(V)	Sb(III)	Sb(V)	
HG-ICP-MS	220	0.32	-	-	-	8.8	-	-	-	(48)
CPE-ETV-ICP-MS	50	-	-	30	-	-	-	4.2	-	(49)
SPME-ICP-MS	60	5.0	5.0			3.2	3.8			(50)
SPE-ICP-MS	300	-	0.21			-	6.8%			(51)
SPME-HPLC-ICP-MS	4.0-19	42	18			3.1-8.7	3.1-8.7			(52)
HG-ICP-MS	-	-	-	4.2	17	-	-	9.04	11.0	(53)
HPLC-ICP-MS	-	-	-	14	12	-	-	-	-	(54)
SFODME-ICP-MS	500	0.18	-	0.37	-	4.7	-	5.9	-	This work

CPE, cloud point extraction; SPME, solid phase microextraction; SPE, solid phase extraction; SPME-HPLC, solid phase microextraction-high performance liquid chromatography; HG, hydride generation; HPLC, high performance liquid chromatography; EF, Enrichment factor; DL, detection limit; RSD, relative standard deviation.

TABLE III
Analytical Results and Recoveries of Analytes in Lake and River Water

Sample	Species	Content (ng mL ⁻¹)	Added (ng mL ⁻¹)	Found (ng mL ⁻¹)	Recovery (%)
Lake water	As(III)	1.57±0.12	1.0	2.52±0.14	95.0
	As(V)	2.56±0.15	1.0	3.61±0.23	105
	Sb(III)	0.37±0.03	1.0	1.31±0.09	94.0
	Sb(V)	1.81±0.10	1.0	2.78±0.16	97.0
River water	As(III)	0.19±0.02	1.0	1.12±0.11	93.0
	As(V)	1.98±0.17	1.0	3.01±0.20	103
	Sb(III)	0.54±0.04	1.0	1.52±0.13	98.0
	Sb(V)	2.31±0.16	1.0	3.26±0.19	95.0

Mean value ± standard deviation, n=3.

200 °C and a pyrolysis time of 20 seconds were selected for the following experiment.

Under the selected drying and pyrolysis conditions, the effect of vaporization temperature on the signal intensity of the analytes was studied with a vaporization time of 4 seconds. The experimental results showed that the signal intensity of the analytes could only be detected at about 800 °C without APDC, and no signal plateau was obtained in the tested vaporization temperature range. However, the situation changed greatly after APDC was

added. A weak signal for As(III)/Sb(III) appeared at 600 °C, the signal increased gradually with an increase in vaporization temperature, and the maximum signal was obtained at 1800 °C for As(III) and 1600 °C for Sb(III), respectively; then the maximum signal was kept constant with a further increase in vaporization temperature up to 2200 °C. Therefore, a vaporization temperature of 2000 °C and a vaporization time of 4 seconds were used in this work.

Analytical Performance

Under the optimized conditions, the linear dynamic range of the calibration curve for this method covered three orders of magnitude with a correlation coefficient better than 0.9951. The detection limits of As(III) and Sb(III), based on three times the standard deviation of the blank solution, were 0.18 pg mL⁻¹ and 0.37 pg mL⁻¹, respectively. The relative standard deviations were 4.7% and 5.9% for As(III) and Sb(III) (n=9, c=0.1 ng mL⁻¹), respectively. Table II lists the performance of reported studies in comparison with the results of the present method (48-54). Generally, the results obtained by the proposed method are either comparable or better than those reported in the literature.

Sample Analysis

The present method was used for the determination of As(III), As(V), Sb(III), and Sb(V) in natural water samples, including lake water and river water. In addition, the recovery experiments of different amounts of analytes were carried out, and the results are summarized in Table III. It can be seen that the recoveries are in the range of 93.0-105%. In order to establish the

TABLE IV
Analytical Results of Analytes in Water Certified Reference Materials

Sample	Element	Found ^a (μg mL ⁻¹)	Certified (μg mL ⁻¹)
Water sample (GSBZ50004-88)	Total As	0.0513±0.0038	0.0479±0.0025
	As(III)	0.0042±0.0003	-
	As(V)	0.0471±0.0038	-
Water sample (GBW(E)080545)	Total Sb	95.7±5.2	100
	Sb(III)	4.3±0.2	-
	Sb(V)	91.4±4.3	-

^aMean value ± standard deviation, n=3.

validity of this method, two certified reference materials of water samples (GSBZ50004-88 and GBW(E)080545), obtained from the Institute for Reference Materials of SEPA (Beijing, P.R. China), were analyzed and the results were found to be in good agreement with the certified value (Table IV).

CONCLUSION

In this paper, a novel method was developed for the simultaneous speciation of inorganic As and Sb by solidified floating organic drop microextraction (SFODME) coupled with electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS), using APDC and 1-undecanol as a chelating reagent and an extraction solvent in SFODME, respectively. At the same time, APDC acted as a chemical modifier in ETV-ICP-MS. The experimental results show that under the selected experimental conditions, the As(III)-APDC/Sb(III)-APDC complex can be extracted effectively with 1-dodecanol and vaporized quantitatively by ETV into the ICP for analysis. In addition, this method provides advantages such as high enrichment factor, low detection limit, simple operation, low cost, good precision and accuracy. It has great potential to be used for the simultaneous speciation of inorganic As and Sb in environmental samples.

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