

A new technique of arsenic determination based on electrolytic arsine generation and atomic absorption spectroscopy

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A method for the determination of traces of arsenic in food has been developed based on electrolytic arsine generation and atomic absorption spectroscopy detection. The essence of the method is the addition of copper and tin salts to the electrolyte solution, enabling a fast and effective arsine evolution. The advantage of this method lies in the fact that it enables the simultaneous concentration of heavy metals, such as cadmium and lead, on cathode. The applicability of the method was illustrated by determining the arsenic content in some food samples based on vegetable oils and by comparing the results with those obtained by the classical technique of chemical hydriding with sodium tetrahydroborate.

Keywords: arsine generation, atomic absorption spectroscopy, electrolysis, trace determination, diffusion rate constants.

INTRODUCTION

The electrolytic generation of arsine (AsH₃) for the purposes of arsenic trace analysis has already been described in the literature. Namely, using a modified Gutzeit method, Oesterberg applied the reduction of arsenic on a cathode in an acid solution in order to determine the arsenic content in biological samples.^{1,2} His method consisted in the electrolysis of a sample solution between platinum foils during 30–45 min. Arsine was evolved together with hydrogen and detected by chemical reaction with mercuric chloride tape. The quantitative determination was carried out by comparing the size of the brown spot developed by the observed sample with that of a standard solution. The use of this method, enabled arsenic concentrations of the order of magnitude of 0.05–5 mg/dm³ were to be determined in digested biological samples. This method suffered the disadvantage of slow arsine generation, disabling the attainment of high concentrations of gaseous arsine. A method of chemical arsine generation with Zn and SnCl₂,³ and NaBH₄,⁴ as reducing agents, combined with AAS arsenic determination, is also known from the literature. This technique enabled 0.002–0.02 mg/dm³ of arsine to be determined,^{4–7} which is superior to the Oesterberg method.

In this paper a refined Oesterberg method is presented, in which the rate of arsine generation was enhanced roughly five times, and atomic absorption spectrometry (AAS) was used for arsine determination instead of mercury(II) chloride tape. The evolution rate enhancement was attained by the addition of copper and tin salts to the electrolyte solution. On account of the enhancement of the evolution rate the detection limit was lowered to 0.002 mg/dm^3 , which is comparable to the detection limit attainable with chemical arsine generation.⁴⁻⁶ However, in comparison to chemical arsine generation, the new electrolytic technique possesses an advantage, that it enables the simultaneous concentration of toxic metals such as cadmium and lead in the deposit on the cathode. Namely, in natural products, arsenic is often just accompanied by cadmium and lead. The applicability of this new technique has already been demonstrated by the simultaneous determination of arsenic, cadmium and lead traces in drinking water⁸ and oil product.⁹

EXPERIMENTAL

Chemicals, p.a. from Merck, As_2O_3 , As(V), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$, NaBH_4 and from Kemika, $\text{NH}_3\text{OHCl} \cdot 2\text{H}_2\text{O}$ and H_2SO_4 were used.

For the stock calibration solution, 1.3203 g As_2O_3 was dissolved in a small volume of 20 % NaOH, neutralized with H_2SO_4 and diluted with demineralized water to the volume 1 dm^3 . Calibration solutions with concentrations in the range $0.02 - 0.2 \text{ mg dm}^{-3}$ were obtained by dilution of the stock solution with 2.6 mol/dm^3 sulfuric acid. These solutions were then modified by addition of copper and tin salts and hydroxylaminehydrochloride.

The samples of 20 g of palm oil, margarine and mayonnaise were prepared in soluble form, suitable for analysis, in two ways: either they were subjected to dry pyrolysis (ashing) in the presence of MgNO_3 ,^{8,10} followed by dissolution of the dry residue in 10 cm^3 2.6 mol/dm^3 H_2SO_4 , or they were subjected to hydrolysis with acid extragent, by boiling for 10 min in 10 cm^3 of 2.6 mol/dm^3 H_2SO_4 containing 0.6 % potassium permanganate and then the aqueous phase was separated and used for analysis (as has been used elsewhere^{11,12}).

The apparatus for electrolytic arsine generation consisted of a cathode and an anode compartment, each 20 cm^3 in volume, separated by a porous glass sinter disc. Both the cathode and anode were of platinum. The cathode was of cylindrical shape with a total surface area of 12.5 cm^2 . A stabilized power supply ($U_{\text{max}} = 12 \text{ V}$ and $I_{\text{max}} = 1.8 \text{ A}$) was used.

The arsenic concentration was measured using Varian Model AAS-275 analyzer. When a solution was to be analysed, it was sprayed into the flame of the analyzer using a standard atomizer. When the cathode gas was to be analysed, it was carried by a stream of argon into the center of a high-temperature ($900 \text{ }^\circ\text{C}$) open silica tube the central axis of which overlapped with the optical path of the analyzer.

RESULTS AND DISCUSSION

Two methods were used for the determination of traces of arsenic in food: those reported by Gutzeit and Oesterberg, based on the chemical or galvanostatic generation of arsine, respectively, with detection by paper strip wetted by mercury chloride solution,^{1,2} and that based on the chemical reduction of arsenic to arsine and the detection of generated arsine by means of atomic absorption spectroscopy.³⁻⁷

The Oesterberg method has a rather high detection limit of 0.05 mg/dm^3 , and thus chemical hydriding coupled with the AAS technique, with a detection limit of 0.002

mg/dm³ is obviously superior. However, an advantage of the electrolytic generation of arsine lies in the fact that a simultaneous concentration of heavy metals in the deposit on cathode occurs. Thus enables a considerable time shortening of the arsenic analysis and the more sensitive flame AAS determination of all heavy metals present in the sample.⁸

Considering the reasons of low sensitivity of the Oesterberg method compared to the method of chemical hydriding, we concluded that it is dealing with the two disadvantages. Firstly, the slow electrolytic generation of arsine does not provide a high enough concentration in the cathode gas, and secondly, the mercurychloride detection is not as sensitive as AAS. In this work, the advantages of both the mentioned methods are combined, by increasing the arsine evolution rate and using AAS for detection instead of mercury(II) chloride. To enable the use AAS, a self-made high temperature silica tube was constructed and placed in the optical path of the spectrometer, through which the cathode gas was conducted.

Firstly the electrolyte solution most suitable for cathodic arsenic hydriding was established and then the new technique was controlled by the determination of arsenic in viands based on vegetable oils.

Optimization of electrolyte composition for cathodic arsenic hydriding

Oesterberg demonstrated that arsenic can be evolved as gaseous arsine (AsH₃) together with hydrogen, by electrolysis of very acidic solutions between platinum electrodes. The evolution is rather slow, which results in a too low concentration of arsine in the cathodic gaseous mixture. Previous investigations showed that cadmium and lead, present in trace concentrations, could not be deposited on cathode, probably due to their fast chemical dissolution. In a search for a possibility of depositing of these heavy metals on the cathode simultaneously with arsenic hydriding, the idea of preserving the traces of deposited heavy metals by alloying them with metals present in macro-concentrations was investigated. A copper/tin alloy to be the matrix in which the traces of heavy metals might be incorporated was tried. Hydroxylaminehydrochloride was already known as an additive that reduces the concentration of oxygen and supports the deposition of tin on the cathode.^{13,14} During the study it was established that deposits of copper/tin on the cathode not only retain traces cadmium and lead, but also enhance the rate of arsine evolution. This discovery was applied to improve the detection limit of arsenic determination, and then to equalize the detection limit with that attained by chemical hydriding by employing AAS.

The influence of additives, copper and tin salts and hydroxylaminehydrochloride to the rate on arsine evolution were investigated by measuring the concentration time dependence during electrolysis of arsenic solutions with various concentrations of additives. All solutions contained 2.6 mol/dm³ sulfuric acid as the supporting electrolyte. In the anode compartment of the electrolytic cell, sodium sulfate was added in a concentration of 1 mol/dm³ to reduce the electrolyte resistance. The composition of the electrolytes in the cathode compartment were as follows:

Solution 1: 15 mg/dm³ arsenic(III)
 0.016 mol/dm³ CuSO₄

	0.75 mol/dm ³ NH ₃ OHCl
Solution 2:	15 mg/dm ³ of arsenic(III)
	0.015 mol/dm ³ CuSO ₄
Solution 3:	15 mg/dm ³ of arsenic(III)
	0.004 mol/dm ³ CuSO ₄
	0.004 mol/dm ³ SnCl ₂
	0.036 mol/dm ³ NH ₃ OHCl
Solution 4:	15 mg/dm ³ of arsenic(V)
	0.04 mol/dm ³ SnCl ₂ ,
	0.036 mol/dm ³ NH ₃ OHCl

The cathode compartment contained 5 cm³ in experiments 1 as 2 and 20 cm³ in experiments 3 as 4. The electrolysis was carried out using a constant current of 1 A.

The time dependence of the arsenic concentration in the electrolyte during electrolysis was measured by spaying the electrolyte solution into the flame of AAS analyzer. Concentration of arsenic of about 5 mg/dm³ was detected by flame AAS with a relative error of about 10 %.

Figure 1 presents the concentration – time dependence in the following linear form

$$Y = -k t + Y_0 \quad (1)$$

where Y is

$$Y = \ln (c/c_0) \quad (2)$$

In Eqs. (1) and (2), c_0 and c are the arsenic concentration at $t = 0$ and at $t > 0$, respectively, and k is the diffusion rate constant $k = 1/(t_{Y=0.63} - t_{Y=0})$.

Equation (1) is a linear form of the Lingane equation.^{15,16}

$$c = c_0 e^{-k t} \quad (3)$$

To prove that the decrease of the arsenic concentration in the solution was completely due to arsine evolution, the cathodic deposit was dissolved after electrolysis and analyzed by AAS. No measurable quantity of arsenic was observed in the deposit. Bearing this in mind, it was calculated according to Suturović¹⁵ that the fraction of arsenic transferred from the solution to the gaseous phase is given by

$$w = 1 - e^{-k t} \quad (4)$$

The experimental results presented in Fig. 1 confirm that the Lingane equation (3) is applicable to the system under investigation, *i.e.*, mass transport appears to be the slow step of arsine evolution.

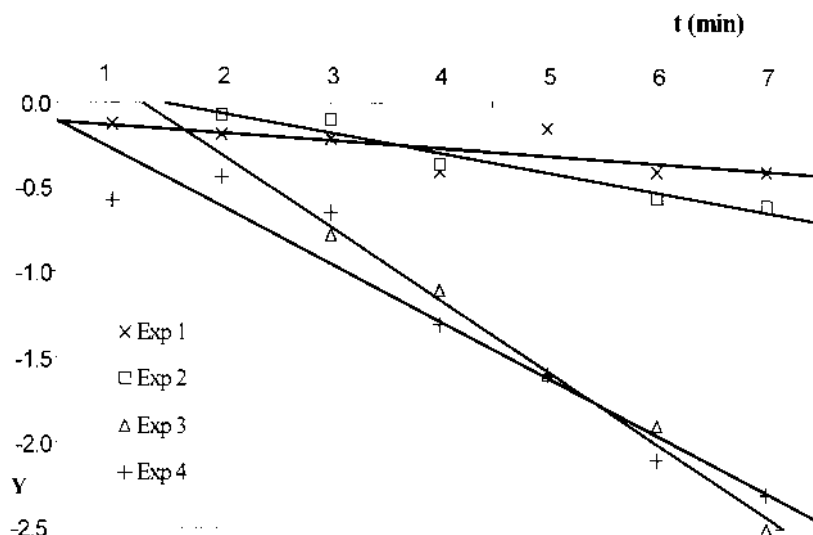


Fig. 1. The decrease of the arsenic concentration electrolysis time for the solutions 1 – 4, presented as the best fit of the linear form $Y = k t + Y_0$

On the basis of Fig. 1, the parameters of the function (1) were determined and are presented in Table I together with the arsine yield data. In principle, the parameter Y_0 in Eq. (1) should be zero, however, its finite scattered value is due to experimental uncertainty. The slopes of the lines are the diffusion rate constants expressed in the units min^{-1} , and can be easily calculated in the units s^{-1} .

TABLE I. The parameters of the function (1) and the arsine yield after 7 min of electrolysis (experimental data and data calculated on the basis of Eq. (4))

	$Y = k t + Y_0$	$w_{\text{calc}} / \%$	$w_{\text{exp}} / \%$
1	$-0.043t + 0.095$	32	37
2	$-0.116t + 0.175$	47	39
3	$-0.420t + 0.544$	99	92
4	$-0.340t + 0.657$	82	90

The diffusion rate constant k in the Lingane equation, at constant potential difference between the electrodes, is related to the diffusion coefficient (D) of the species containing arsenic, and to the thickness of the diffusion layer (δ), by the formula

$$k = (A D) / (V \delta) \quad (5)$$

where A is cathode area and V is the volume of catholyte. According to this equation, k depends inversely on the thickness of the diffusion layer and enables it to be calculated. However, this calculation is outside the scope of this work.

The results presented in Fig. 1 and in Table I demonstrate that with the solutions 1 and 2, with only a copper salt, or a copper salt plus hydroxylaminehydrochloride as additives, the arsenic concentration decreases at a rather low rate. By adding copper(II)

sulfate, tin(II) chloride and NH_3OHCl simultaneously in the concentrations 0.004, 0.04 and $0.036 \text{ mol dm}^{-3}$, respectively, a remarkable acceleration of decrease of the arsenic concentration became obvious. Namely, with such an electrolyte composition, after only 7 min of electrolysis, the arsenic concentration in the solution dropped to a practically unmeasurable value. Therefore, such a composition of the electrolyte solution was used for further arsenic determinations.

The determination of arsenic in viands based on vegetable oils

The applicability of the improved technique of arsenic determination involving the generation of arsine on the cathode is demonstrated on the examples of arsenic determination in viands based on vegetable oils: palm oil, margarine and mayonnaise.

The calibration solutions, were made of 2.6 mol/dm^3 sulfuric acid to which 0.004 mol/dm^3 copper(II) sulfate, 0.04 mol/dm^3 tin(II) chloride and 0.036 mol/dm^3 hydroxylamine-hydrochloride and small volumes of standard arsenic solutions were added.

By measuring the arsine concentration in the cathode gas, arsenic was determined using the heated silica tube mentioned in the experimental section. The arsine peak areas were measured for blank solution (a) and for calibration solutions containing arsenic in the concentrations 0.02, 0.05 and 0.1 mg/dm^3 , (b, c i d). The forms of the

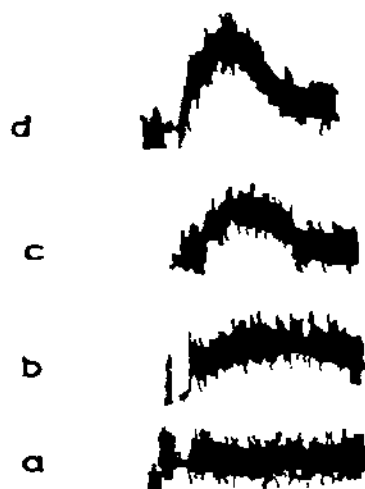


Fig. 2. The arsenic AAS peaks used for instrument calibration: that of the blank solution (a) and those of the calibration solutions containing arsenic in the concentrations: 0.02 (b), 0.05 (c) and 0.1 mg/dm^3 (d).

AAS peaks are presented in Fig. 2.

The calibration peak areas (P) were calculated using the peak areas recorded after each of 6 min of electrolysis, after subtraction of the base line, according to the formula:⁸

$$P = \frac{\sum_{i=2}^5 P_i}{4} \frac{P_1}{P_6}$$

The peak areas calculated for each concentration are presented in Table II.

TABLE II. Calibration data for AAS arsenic determination

Arsenic content/mg dm ⁻³	Blank	0.02	0.05	0.10
<i>P</i> (int. unit)	192	665	1411	2861

For the calibration represented by the equation $P = 44.2 + 26778 c$, the correlation coefficient was determined to be 0.9989.

With the optimized solution composition, the detection limit was found to be 0.002 mg/dm³ (the triple standard deviation for ten repetition of AAS detection of added 0.02 mg/dm³ arsenic and blank). The arsenic detection limit of the new electrolytic technique was identical to the detection limit of chemical hydriding with AAS detection.⁷ However, the advantage of the applied electrochemical hydriding is the enlarged range of linearity of the signal vs. concentration dependence. With chemical hydriding, the calibration curve deviated from linearity, with a decrease of sensitivity at arsenic concentrations above 0.02 mg dm⁻³. The new electrolytic technique enables an enhancement the sensitivity of the determination of arsenic above 0.02 mg dm⁻³ and to handle larger samples.

After calibration of the instruments, comparative arsenic determinations in food, palm oil, margarine and mayonnaise using both chemical and electrochemical arsenic hydriding with AAS detection were performed. The results of the analysis were presented in Table III.

TABLE III. The arsenic peak areas obtained by AAS after chemical hydriding of solutions of dry-ashed samples (P_1) and of acid treated samples (P_2), and those obtained after electrochemical hydriding of dry-ashed samples (P_3). The corresponding concentrations are designated as C_1 , C_2 and C_3

Samples	Blank	Palm oil	Margarine	Mayonnaise
P_1^* / int. units	410	–	164	131
P_2^* / int. units	832	627	931	840
P_3^{**} / int. units	5400	5397	1875	1441
C_1 / mg kg ⁻¹	0.07	0.07	0.07	0.13
C_2 / mg kg ⁻¹	0.051	0.089	0.023	0.030
C_3 / mg kg ⁻¹	0.002	0.090	0.021	0.031

* Standard addition 0.02 mg dm⁻³; ** Standard addition 0.2 mg dm⁻³

The last two rows of Table III show a fair agreement between the results obtained by the chemical hydriding and by the new electrochemical hydriding technique. Inspection of the data for the P_1 and P_2 rows, and the C_1 and C_2 rows, reveals a further advantage of the electrochemical over the chemical hydriding technique, relating namely, to the influence of sample preparation on the sensitivity. When dry-ashed samples of margarine and mayonnaise were analyzed using chemical hydriding, lower sensitivity (P_1) for small standard additions was evidenced than with the samples treated by hydrolysis with sulfuric acid (P_2). On the contrary, electrolytic generation of arsine after dry-ashing sample pretreatment enabled an increased sensitivity of determination by using enlarged masses and standard additions.

CONCLUSION

An electrolyte solution containing 0.004 mol/dm³ CuSO₄, 0.04 mol/dm³ SnCl₂, and 0.036 mol/dm³ NH₃OHCl in 2.6 mol/dm³ H₂SO₄ was shown to be suitable for electrolytic arsenic hydriding, enabling sensitive arsenic determination in food samples. The detection limit of 0.002 mg/dm³ attained with this electrolyte solution is equal to the detection limit attained with the previously used chemical hydriding technique. The new technique possesses the following advantages: it enables the simultaneous concentration of heavy metals on the cathode, it shows an enlarged range of linearity of the peak area vs. concentration dependence so its sensitivity does not decrease with increasing mass of the analyzed samples. The new AAS technique with electrolytic arsine generation was illustrated on the practical examples of the analysis of the arsenic contents in viands based on vegetable oils and fair agreement was attained with the method of chemical hydriding using sodium tetrahydroborate.

ИЗВОД

НОВА ТЕХНИКА ЗА ОДРЕЂИВАЊЕ АРСЕНА ЗАСНОВАНА НА ЕЛЕКТРОЛИТИЧКОМ ГЕНЕРИСАЊУ АРСИНА И АТОМСКОЈ АПСОРПЦИОНОЈ СПЕКТРОСКОПИЈИ

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Развијена је нова метода за одређивање трагова арсена у храни заснована на електролитичком генерисању арсина. Срж методе је додавање соли бакра и калаја у електролит, а што омогућава ефективно издавање арсина. Применљивост методе илустрована је одређивањем садржаја арсена у биљном уљу и поређењем резултата са оним добијеним класичним техникама хемијског хидрирања натријум-тетрахидроборатом

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