

Potentiometric Sensor for Trace Level Analysis of Copper Based on Carbon Paste Electrode Modified With Multi-walled Carbon Nanotubes

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It is here established that potentiometric carbon paste electrodes (CPE) modified with multi walled carbon nanotubes (MWCNT) are useful analytical tools for copper ion determinations. MWCNTs are incorporated into the composition of CPE to decrease the ohmic resistance. The selectivity of CPE is modified by applying the copper(II) ionophore I as recognition element. To optimize the method, sensor response is evaluated by changing the CPE composition and pH of the sample solution. The suitable selectivity coefficient is obtained for the CPEs compare to interfering cation. The Nernstian slope and detection limit are achieved 28.4 mV/decade and 1.1×10^{-6} M Cu^{2+} , respectively. The electrode shows a wide dynamic linear range for Cu^{2+} from 10^{-6} to 10^{-2} M. The sensor displays a short response time of 1.05 s. Finally, a number of native and spiked drinking water samples are potentiometrically assessed for copper and the results compared with atomic absorption spectroscopy (AAS). The result of presented sensor is in agreement with the result of AAS for acidified sample solution.

Keywords: copper ion; carbon paste electrode; multi-walled carbon nanotubes; potentiometry;

1. INTRODUCTION

Copper is an essential element in low concentration and is also toxic at high concentration. [1] The occurrence of copper in environment is widespread as is used for many industrial, agricultural and domestic purposes. It is known to cause gastrointestinal, cataract, Wilson disease, cancer, hypoglycemia and dyslexia. [2] Reactivity and biological uptake of copper are strongly influenced by its free ion concentration.

In view of such toxic effects of copper, its determination in environmental samples is thus important. A number of methods, such as atomic absorption spectrometry (AAS) [3-5], cold vapour

AAS or flame atomic absorption spectrometry–electrothermal atomization (AAS-ETA) [6-8], inductively coupled plasma-optical emission spectroscopy (ICP-OES) [9, 10], anodic stripping voltammetry [11-13], chromatography [14, 15], gravimetric detection [16] or photometry [17] are used for its determination at low concentration level. Moreover, all these methodologies require a complex and expensive apparatus and this hinders their use for routine in Clinical Chemistry laboratories. [18] It is well known that the toxicity of this metal is attributed to “free cupric ion” rather than inorganic and organic complexes. [19] Potentiometric measurement with a copper selective electrode allows directly determination of free copper ion concentration in water samples. [20, 21]

Potentiometric measurements using ISEs are a simple, economic, selective, precise and rapid method of analysis, which have found applications in different fields. Ion-selective electrodes (ISE) are an important analytical tool designed to respond to a particular ion in solution, usually the free metal ion. The potentiometric methods employed different kind of ISEs which are composed of glass electrode, liquid membrane electrode, ion exchanger electrode, neutral carrier electrode and solid state electrode. Polymeric membrane and carbon paste electrodes are the most popular, robust and general electrode in the potentiometric field. [1, 19] The CPEs have some advantages against potentiometric sensors based on polymeric membranes as its easy construction and regeneration. The CPEs are cheaper than polymeric membrane and they display more stable electrochemical response and lower ohmic resistance. Potentiometric electrodes based on carbon paste matrix have been used with suitable analytical results to determine copper. Carbon pastes have been employed for the fabrication of potentiometric electrodes since 1970s. In these sensors, the selective agent is incorporated into the carbon paste matrix by mixing it with carbon powder and paraffin oil. [22]

The carbon nanotubes (CNTs), since their discovery by Iijima in 1991, have attracted considerable attention due to their fascinating and unique structural, low resistivity, large surface area, mechanical, electrical and electrochemical properties. The combination of these characteristics makes CNTs unique materials with capability to promote electron transfer reaction and improve sensitivity in electrochemistry, and thus they are widely used to prepare modified electrodes. [23, 24] Moreover, the potentiometric determinations of inorganic and organic compounds are improved by incorporating CNTs into the structure of CPE electrodes. [25-28]

In this work, we introduce a novel potentiometric sensor for selective monitoring of trace amounts of copper in various samples. The purpose of the present work is to obtain a better selective modified electrode based on carbon paste electrode modified with MWCNTs for Cu^{2+} ion. This sensor is easily prepared and applied. It can be blend with graphite and paraffin oil to make a very highly reproducible copper ion selective electrode. The present work describes the construction, potentiometric characterization, and analytical application of a carbon paste modified with MWCNTs.

2. EXPERIMENTAL SECTION

2.1. Reagents

Copper(II) ionophore I was purchased from Sigma-Aldrich company. Graphite, paraffin, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, NaCl, KCl, PbCl_2 , ZnCl_2 and CdCl_2 were purchased from Merck (Darmstadt,

Germany). The multi-walled carbon nanotubes MWCNTs (OD 10-20 nm, ID 5-10 nm, length 5-15 μm , Purity 95%) was of Shenzhen (China). A copper wire was obtained from Simcat Company (Tabriz, Iran). Stock solution of Cu^{2+} (1M) was prepared by dissolving 17.04 g of copper chloride in 100 mL of double distilled water.

2.2. Apparatus

Electrochemical data is obtained with a two-electrode system using an Autolab PGSTAT 101 (Metrohm Autolab, Utrecht, The Netherlands) managed by NOVA software. A saturated calomel electrode (Azar Electrode Co., Teheran, Iran) is used as the reference electrodes. A B2000 pH meter equipped with a GCFC 11 combination glass electrode is used for pH measurements (Orion, thermo scientific, USA). Determination of copper is performed with a flame atomic absorption spectroscopy GBC model 902AA (GBC Scientific® Equipment, Dundenong, Vic., Australia) using an air–acetylene flame. A copper hollow cathode lamp is used as a light source at 324.7 nm and 0.5 nm band width. All glassware containers are carefully treated with 2.0 M nitric acid (guaranteed reagent) and rinsed with double distilled water.

2.3. Preparation of the CPE

In order to prepare CPE sensors, certain amount of graphite, copper(II) ionophore I and MWCNTs is homogenized in a mortar. After that, paraffin is melted in a dish by a calibrated heater at 45–50 $^{\circ}\text{C}$. Subsequently the mixture of graphite and copper ionophore is added to the melted paraffin and homogenized with a stainless steel spatula. This prepared paste is used to fill electrode which made of a glass tube (ID of 5mm and a height of 12 cm). A copper wire (15 cm length, 0.4 mm outer diameter) is inserted to the composite at the end of the electrode body. After cooling at room temperature, the electrode surface is burnished on a paper to remove the residual particles (see, Figure 1). Afterward, the CPEs are conditioned in the 10^{-3} M copper ion solution for 48 hours.

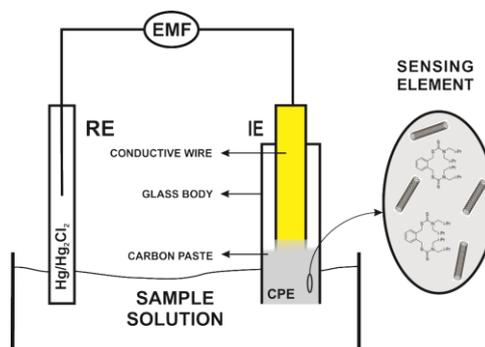


Figure 1. Schematic illustration of sensing element in the carbon paste matrix (on the right) and CPE as an indicator electrode (IE). General protocol to determine copper ion (on the left). The sensor is placed into the electrochemical cell and the free copper ion is quantitatively measured by potentiometric method.

2.4. General method for potentiometric determination of copper

All electromotive forces (EMF) are measured at room temperature (21 ± 5 °C) in stirred solutions. A double-junction Hg/Hg₂Cl₂/4 M Cl⁻ reference electrode (RE) is employed. Activity coefficients are calculated using the Debye–Huckel approximation and the potential measurements are corrected by using the Henderson equation to determine the liquid junction potential (see, Figure 1).

2.5. Real samples

About 100 ml of tap water sample is adjusted to an optimum pH 5 by adding diluted sodium hydroxide or nitric acid. The CPEs are inserted in to the real water sample to determine copper ion concentration and subsequently copper solution is added at 3 levels of concentrations.

3. RESULTS AND DISCUSSION

Copper sensors based on the CPE modified with MWCNTs are applied here and their detection limits reached trace levels. The MWCNTs are incorporated to the carbon paste composition to decrease ohmic resistance. The CPE compositions are chosen with a small concentration of ionophore (5%) to prepare the sensor. The CPE with low concentration of ionophore is expected to induce smaller counter diffusion fluxes and therefore, improved detection limits, but could exhibit deteriorated selectivity, which would have an adverse effect. The copper sensor is applied in the environmental analysis at low cost and can easily determine copper concentration in tap water samples.

3.1. The pH dependence of the electrode response to Cu²⁺

With trace analyses of heavy metal ions in environmental samples, the sample pH must often be controlled. At the rather low pH values required to avoid complex formation of the investigated metal ions, H⁺ is often the dominant interfering ion. Hydrogen ions are known to cause interference in the performance of the sensors. [29] Thus, it is important to determine useful pH range where the sensor can perform without being affected by H⁺ ions. At the other hand, copper may be charged (free ion) or neutral (copper hydroxide) depending on pH. [30] The interactions between copper and surface of CPEs are attributed to the synergy of electrostatic forces which are strongly affected by the pH level. [1, 31-33]. The pH influence on the potentiometric responses are tested in 1×10^{-3} M copper solutions (Figure 2). Small volumes of nitric acid or sodium hydroxide solutions are added to adjust the pH values. The potential measurement is read when it is steady, after addition of acid or base, and pH measurement is made. In the presence of Cu²⁺, there is no pH influence on the electrode response for pH values in the range of 3 to 5.5. The potential decreases in the CPE at pH higher than 6 due to the hydrolysis of Cu²⁺ to form copper hydroxide. The hydroxyl formation significantly reduces the measured activity of free Cu²⁺.

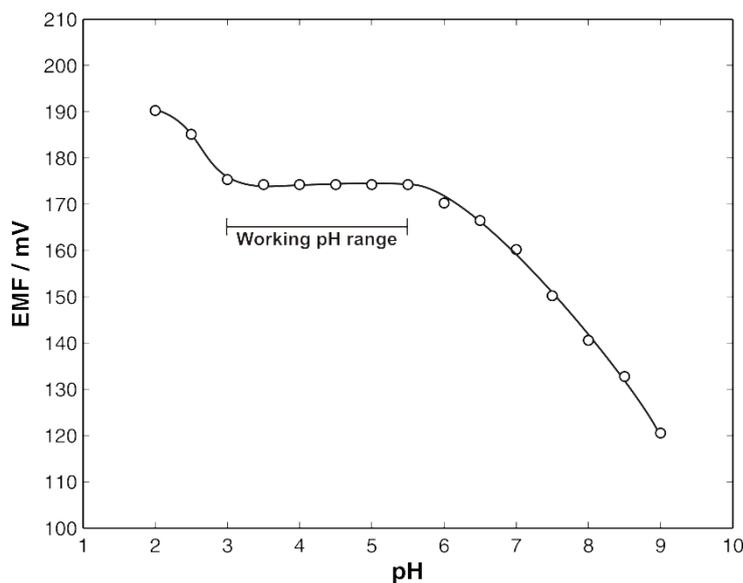


Figure 2. Potentiometric responses of the CPE in 1×10^{-3} M copper ion solutions at several pH values.

The EMF response increases at pH lower than 3 according to the interference effect of proton. The suitable working pH range for the sensor is 3 to 5.5 because in this range CPEs shows the Nernstian potentiometric response which is in agreement with the previous discussion.

3.2. Calibration curve and potentiometric response

This paper introduces a novel direction for potentiometric sensing, termed calibration potentiometry. The response of CPEs is usually dominated by the phase boundary potential at the membrane/sample interface. In direct potentiometry, the magnitude of the measured potentials is used to determine the composition of the sample. Calibration potentiometry allows obtaining information on the composition of an unknown sample on the ISE membrane. [34, 35]

Surface of CPEs separates the sample from the electrode and the electromotive force between reference electrodes in the aqueous sample and the CPEs is measured under zero current conditions. It is an extremely simple and direct form of converting chemical into electrical information. The logarithmic activity of the ion of interest is directly proportional to the observed electromotive force, or potential. In so-called direct potentiometry, this measurement is performed directly on the sample, ideally without any sample preparation steps that are often impossible in remote sensing situations. [36-39]. Copper-selective electrode with linear dynamic range of 10^{-6} to 10^{-2} M is reported here to measure copper in unbuffered solution. In the absence of interferences, the EMF observed with CPEs is a logarithmic function of the bulk sample activities and can be described by the Nernst equation. In most cases, deviations from such a response can be either explained by activity changes in the organic membrane surface layer or by differences between the sample activities in the bulk and the membrane surface layer. The electrodes still respond according to the Nernst equation, which is dependent on the sample activity at the phase boundary, but not in the solution bulk.

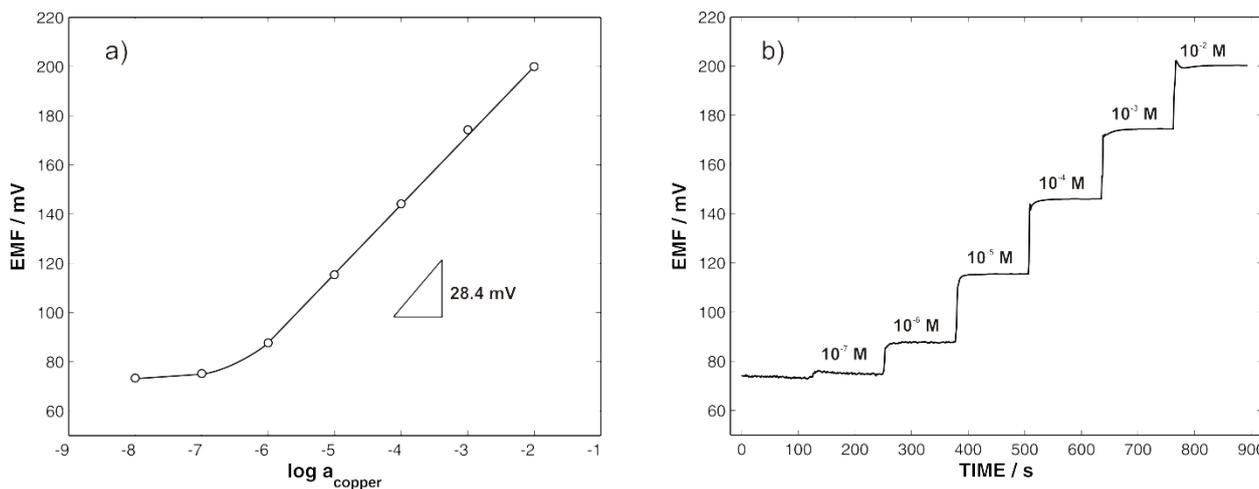


Figure 3. Response of CPEs modified with MWCNTs to unbuffered copper chloride solutions obtained by serial dilution of copper sample. a) Potentiometric response of copper selective electrodes determined in a background of deionized water; the lower and upper detection limit are 10⁻⁶ and 10⁻² M, respectively. The CPE contains 5% copper(II) ionophore I, 5% MWCNTs, 30% paraffin and 60% graphite. b) Time trace of the EMF response of a copper-selective electrode in the range of 10⁻⁸ to 10⁻² M copper sample.

Under such conditions, the potentiometric response is a function of zero-current ion fluxes to or from the membrane surface. In this work, the behavior of CPEs in the different concentration range of copper ion is investigated. Their calibration curves and potentiometric plot with unbuffered solutions are shown in Figure 3. The CPEs with 5% of copper(II) ionophore I as a recognition element has an apparently Nernstian response with 28.37 mV/decade slope in the calibration range.

3.3. Selectivity study

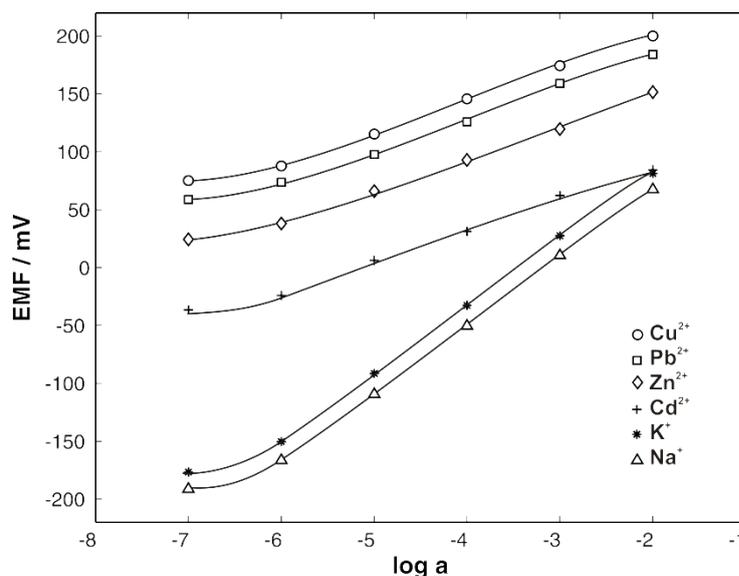


Figure 4. EMF responses of copper selective CPEs containing copper(II) ionophore I conditioned in 10⁻³ M NaCl toward the chloride salts of the cations Cu²⁺, Pb²⁺, Zn²⁺, Cd²⁺, Na⁺ and K⁺.

For selectivity measurements, the CPEs are conditioned in a discriminated ion solution. As established recently, this has a beneficial effect because it avoids any possibility of primary ion leaching from the electrode. The chloride salts of different cations are measured at varying concentrations in the order of increasing preference by the sensor (see, Figure 4). Indeed, CPEs with low concentration of active components exhibits suitable copper selectivity. [40]

The equation 1 shows that the Nicolskii coefficient, K_{IJ}^{pot} , as determined with separate solutions, is expected to be a constant parameter for a particular ISE. As long as the EMF follows the Nernstian function for every ion under consideration, K_{IJ}^{pot} should be independent of the sample activities. With these respects, the Nicolskii coefficient is indeed a useful characteristic of any particular ISE. Equation 1 is used to calculate the selectivity coefficient by inserting the Nernstian equation for both primary and interfering ion [41] (where K_{IJ}^{pot} is the selectivity coefficient, E_J^0 is defined for the interfering ion in complete analogy to E_I^0 for the primary ion according, Z_I is the charge of the primary ion to eq (1):

$$K_{IJ}^{\text{pot}} = \exp\left(\frac{Z_I F (E_J^0 - E_I^0)}{RT}\right) \quad (\text{eq. 1})$$

The obtained logarithmic values are reported for Pb^{2+} , Cd^{2+} , Zn^{2+} , Na^+ and K^+ . The slopes of potentiometric response are closed to the Nernstian response for all of the interfering ions. These results are in agreement with earlier reports on ionophore-based systems that showed the selectivity coefficients can be obtained either by conditioning the membranes with an interfering ion (see, Table 1).

Table 1. Experimental selectivity coefficients for Cu-selective CPEs containing 5% copper(II) ionophore I.

Ion	Slope (mV/decade)	Intercept (mV)	$\log K_{IJ}^{\text{pot}}$
Pb^{2+}	28.2	240.8	-0.6
Zn^{2+}	28.1	206.1	-1.8
Cd^{2+}	27.3	141.1	-3.9
Na^+	58.8	185.52	-2.5
K^+	58.2	199.7	-1.9

3.4. Detection Limit

ISE has a lower and upper detection limit where the response starts to deviate significantly from a Nernstian electrode slope. Generally, they fall into activity ranges where the electrode starts to loose sensitivity toward the primary ion. According to the IUPAC recommendation of 1976, the

detection limit is defined by the cross section of the two extrapolated linear calibration curves. According to the Figure 3a, the lower detection limit are 1.07×10^{-6} M of copper ion. [41]

3.5. Response time

In IUPAC recommendations, it is defined as the length of time between the instant at which the ISE and a reference electrode are brought into contact with a sample solution (or the time at which the concentration of the ion of interest in a solution is changed on contact with an ISE and a reference electrode) and the first instant at which the potential of the cell becomes equal to its steady state value within 1 mV or has reached 90% of the final value. [41] The CPE shows the fast response time toward the copper ion and the response time is 1.05 s.

3.6. Short and long time stability

Time stability is the stability of the analytical response over a short or long interval of time. To measure the time stability, the ISEs are placed into the potentiometric cell in determined concentration in the calibration range and subsequently the slope of EMF versus concentration is calculated. The slope of the potentiometric time trace is measured for 1 and 24 hours to report the short and long time stability, respectively. [41] The time stability of the copper selective CPEs is 1.2 mV/h.

4. APPLICATION

As a more practical example, Table 2, also lists the concentration of copper in the tap and river water sample of Iran. The copper ion concentration is determined in real water samples by using copper selective CPEs and AAS analysis as reference method in order to verify the validation of the presented method.

Table 2. Determination of copper ion in real water samples, Conditions: The measurement is performed at optimum effective parameters.

Sample	Added Cu^{2+} (M)	Found Cu^{2+} (M) by CPEs	Found by AAS
Tap water Qazvin	5.0×10^{-6}	5.1×10^{-6}	4.9
Tap water Karaj	5.0×10^{-6}	4.8×10^{-6}	4.7
River water Karaj	5.0×10^{-6}	4.2×10^{-6}	4.8

To validate the sensor, standard solutions of copper nitrate are prepared and the standard calibration curve of copper by using AAS analysis is plotted. The result of AAS calibration gives a total copper level. In contrast to an external calibration with CPEs that gives a free concentration of

copper ion. As expected, the total and free ion concentrations are practically the same in the acidified water sample solution. The results of the proposed method are closed to the obtained results of the reference method.

5. CONCLUSION

The potentiometric methodology based on CPE introduced here provides a convenient ion analysis of the sample without requiring complex instrumentation. MWCNTs are incorporated into the composition of CPE to decrease the ohmic resistance. The selectivity of CPE is modified by applying the copper (II) ionophore I as recognition element. Ionophores ordinarily used in direct potentiometry with ion-selective electrodes can be applied for the direct measurement of so-called free ion concentrations. Concentrations in the range of 10^{-7} to 10^{-2} M copper ion can be determined by this method. The examples of this methodology include the determination of copper ion in real water samples. Matrix effects are not found to be important for complex samples such as real water samples that also contain complexing agents. In table 3, the CPE is compared with other sensors and methods previously reported, regarding some analytical characteristics. The CPE sensor displays suitable limit of detection (LOD) and wider linear dynamic range (LDR).

Table 3. Comparison of developed sensor with other sensors and methods previously reported.

Method	LOD (M)	LDR (M)	Reference
Presented method	1.1×10^{-6}	$1 \times 10^{-6} - 1 \times 10^{-2}$	-
POT-PVC	4.4×10^{-6}	$4.4 \times 10^{-6} - 1.0 \times 10^{-1}$	[42]
POT-PVC	4.8×10^{-7}	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	[43]
POT-CPE	1×10^{-8}	$1.0 \times 10^{-8} - 1.0 \times 10^{-1}$	[44]
POT-CM-CPE	7×10^{-7}	$9.8 \times 10^{-7} - 7.6 \times 10^{-2}$	[20]
POT-FIA	4.6×10^{-8}	$6.4 \times 10^{-7} - 2.0 \times 10^{-4}$	[19]
CV-MIP-CPE	2.3×10^{-8}	$1.0 \times 10^{-6} - 1.0 \times 10^{-4}$	[45]
CV-zeolite -MWCNT/GCE	1.1×10^{-8}	$5.0 \times 10^{-8} - 1.0 \times 10^{-5}$	[27]
ASV-CPE-Chitosan	1.0×10^{-8}	$7.9 \times 10^{-8} - 1.6 \times 10^{-5}$	[26]
ASV-Antimony-CPE	1.7×10^{-8}	$1.7 \times 10^{-8} - 1.6 \times 10^{-6}$	[46]
ASV-SWV-CPE	3.0×10^{-9}	$5.0 \times 10^{-8} - 2.0 \times 10^{-7}$	[47]
DP-ASV-MWCNTs-GC	1.5×10^{-11}	$1.5 \times 10^{-11} - 2.3 \times 10^{-8}$	[28]
AV-MWCNTs-CPE	8×10^{-12}	$2.0 \times 10^{-11} - 4.0 \times 10^{-7}$	[48]
AAS	3.2×10^{-10}	$1.0 \times 10^{-8} - 6.3 \times 10^{-5}$	[49]

CV: Cyclic voltammetry, ASV: Anodic stripping voltammetry, DPV: Differential pulse voltammetry, GC: Glassy carbon, AV: Adsorptive Voltammetry, Potentiometry: POT, CM: Chemically modified, FIA: Flow injection Analysis, AAS: Atomic absorption spectroscopy.

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