

Determination of phosphorus content in marine sediment samples using inductively coupled plasma-optical emission spectrometry (ICP-OES) technique after microwave-assisted aqua regia digestion

Oznaczanie zawartości fosforu w próbkach osadu morskiego z wykorzystaniem techniki optycznej spektrometrii emisyjnej ze wzbudzeniem w plazmie indukcyjnie sprzężonej (ICP-OES) po rozkładzie za pomocą wody królewskiej wspomaganym promieniowaniem mikrofalowym

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Abstract: A method for the determination of phosphorus content in marine sediment samples using ICP-OES technique has been developed. A microwave-assisted aqua regia digestion has been applied for sediment sample dissolution. The method was optimized then its validation parameters were calculated. Assessing the selectivity found the spectral interferences from other elements (especially copper) can be partially eliminated by using the optimal operating conditions. The method exhibited excellent linearity ($r > 0.999$) in the entire measurement range (25–5000 mg P kg⁻¹). It was also characterized by high repeatability (coefficient of variation of 1%) and very good recovery (98%). The low expanded uncertainty (<10%) was associated with a high concentration of phosphorus in the marine sediment samples examined.

Keywords: phosphorus, marine sediment, inductively coupled plasma-optical emission spectrometry, microwave-assisted digestion

Streszczenie: Opracowano metodę oznaczania zawartości fosforu w próbkach osadu morskiego z wykorzystaniem techniki ICP-OES. Do rozтворzenia próbek osadów zastosowano rozkład za pomocą wody królewskiej wspomaganą promieniowaniem mikrofalowym. Metodę zoptymalizowano, a następnie wyznaczono jej parametry walidacyjne. Oceniając selektywność stwierdzono, że interferencje spektralne ze strony innych pierwiastków (szczególnie miedź) mogą być korygowane przez zastosowanie optymalnych warunków pomiaru. Metoda wykazała doskonałą liniowość ($r > 0.999$) w całym zakresie pomiarowym (25–5000 mg P kg⁻¹). Ponadto charakteryzowała się wysoką powtarzalnością (współczynnik zmienności 1%) oraz bardzo dobrym odzyskiem (98%). Niska niepewność rozszerzona (<10%) była związana z wysoką zawartością fosforu w badanych próbkach osadu morskiego.

Słowa kluczowe: fosfor, osad morski, optyczna spektrometria emisyjna ze wzbudzeniem w plazmie indukcyjnie sprzężonej, rozkład wspomaganą promieniowaniem mikrofalowym

Introduction

Phosphorus is a key component of fertilizer, so it is crucial for the world's food supplies. It is intensively involved in both terrestrial and marine biogeochemical cycles. This element is a potentially limiting nutrient that sustains primary productivity and it has been recognized as a key factor responsible for eutrophication in lake, estuarine and some other waters. The excessive supply of phosphorus to water systems, cause a degradation of their quality through the proliferation of algae, thus hindering various water uses. Phosphorus in water from external origins comes from natural and agricultural diffuse sources or point sources (industrial and domestic effluents). Sediments, as an internal source of phosphorus can contribute phosphate to the overlying waters at levels comparable to the external source. To evaluate the risk of eutrophication in aquatic systems it is necessary to know the phosphorus distribution among the different sediment phases [1]. The popular colorimetric methods for determining phosphorus content in soil and sediment samples are increasingly replaced to inductively coupled plasma-optical emission spectrometry (ICP-OES). The main reason is the growing critical attitude to the colorimetric measurement, resulting from the profound impact of interferences on the phosphorus determination and the advantages of ICP-OES. The standard test method is time consuming and expensive; however, ICP-OES offers a quick and simple method for determination of phosphorus content in sediment samples [2].

The purpose of this research was to develop a method for determining the phosphorus content in marine sediment samples by ICP-OES technique. Marine sediment samples were converted into solution by microwave-assisted aqua regia digestion. The method was optimized and the main objective of this study was to calculate its validation parameters. Within the framework of the validation process, selectivity, linearity, limit of detection, limit of quantification, range, repeatability, intermediate precision, reproducibility and trueness have been described in this paper. The expanded uncertainty of sediment sample analysis with an ICP-OES technique also was assessed.

Experimental

Reagents and calibration

Hydrochloric acid HCl (36%, Tracepur, Merck) and nitric acid HNO₃ (65%, Emplura, Merck) in the ratio of 3:1 (v/v HCl to HNO₃ as aqua regia) were used to prepare each blank, sample and standard solution. Standard solutions at six concentration levels: 0.5, 2.0, 10, 20, 50, 100 mg P dm⁻³ were prepared by diluting a 1000 mg dm⁻³ standard phosphorus solution (ICP standard-1000 mg P dm⁻³, concentration 1001±2 mg dm⁻³ in 2% HNO₃, Ultra Scientific, Inc., USA), then adding 36 cm³ of HCl and 12 cm³ of HNO₃ into 100 cm³ volumetric flasks and bringing up to full volume with deionized water.

Tab. I. Optima 2000 DV operating conditions.

Plasma gas flow	16 dm ³ min ⁻¹
Auxiliary gas flow	0.2 dm ³ min ⁻¹
Nebulizer gas flow	0.7 dm ³ min ⁻¹
RF power	1450 W
Plasma view	Radial
Read delay	60 sec
Peristaltic pump flow rate	1.5 cm ³ min ⁻¹
Spray chamber	Cyclonic
Processing mode	Peak area or Peak height
Nebulizer	Peek Mira Mist
Injector	Alumina 2.0 mm i.d.
Sample tubing	Standard 0.76 mm i.d.
Drain tubing	Standard 1.14 mm i.d.
Quartz torch	Single slot
Sample capillary	PE 0.58 mm i.d.
Replicates	3

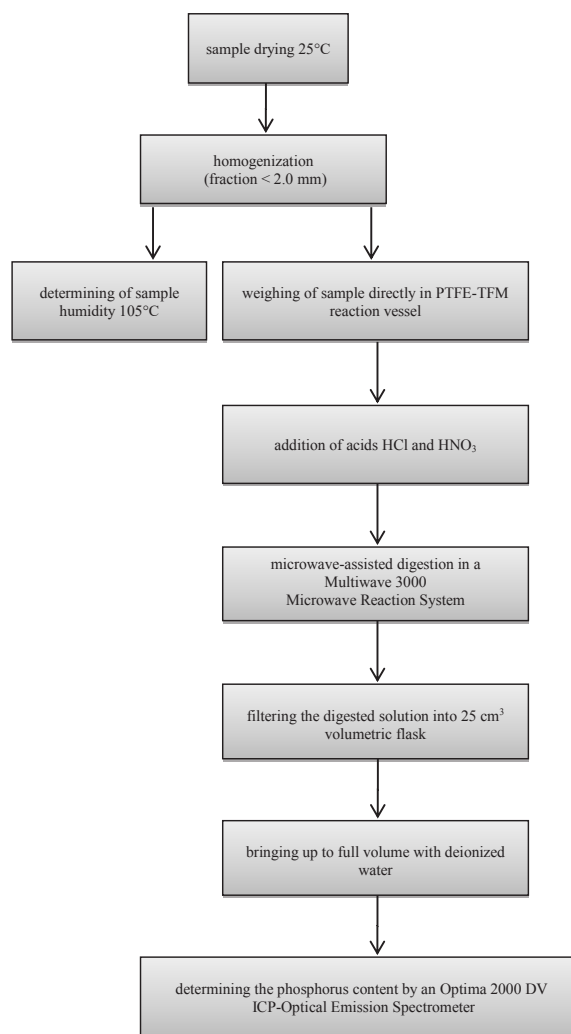


Fig. 1. Analytical procedure scheme for the determination of phosphorus content in sediment samples by ICP-OES technique.

Equipment

A Multiwave 3000 Microwave Reaction System (Anton Paar, Graz, Austria) was used for sample digestion. The measurements (of two P lines at 213.617 nm and 214.914 nm) were performed using the PerkinElmer Optima 2000 DV ICP-Optical Emission Spectrometer (PerkinElmer, Inc. Shelton, CT, USA). Optima 2000 DV operating conditions were presented in Tab. I.

Analytical procedure

Solid sample preparation in ICP-OES technique is more complex than liquid, because they must be converted into solution before analysis. This stage usually encompasses grinding and acid digestion. The aqua regia digestion (3:1 v/v HCl to HNO₃) is the most commonly used sediment sample preparation [3, 4]. It can be conducted with flasks fitted with reflux condensers in an opened system [5], microwave-assisted digestion in a closed system [6, 7, 8] or other [9]. The first one is very tedious and time consuming [10]; however, digestion in a closed microwave system is a rapid, safe, and efficient procedure [11]. In this research, samples of certified reference material (PACS-3, Marine Sediment Certified Reference Material for Trace Metals and other Constituents, National Research Council, Canada) were used for test results, so mechanical sample preparation was not necessary. However, the standard mechanical sample preparation is based on sieved to remove coarse material (≥ 2 mm) and homogenized in a mortar grinder (after sample drying at 25°C). A sample to be analyzed was drawn of 0.5 g and weighed out in the 100 cm³ PTFE-TFM reaction vessel then 9 cm³ of hydrochloric acid and 3 cm³ of nitric acid were added. The vessel was allowed to react for 15 minutes prior to sealing it. A vessel was closed with integrated release valve and safety disk fixed in a screw cap then placed into ceramic jacket. The complete reaction vessel was placed in the rotor then in the microwave. In this case, the used program was as follows: 10 min for reach 1400 W of power, held for 15 min and 10 min for cooling. Simultaneously, the sediment humidity (at 105°C) was determined. After digestion procedure, the digested solutions were filtered through quantitative filter papers (grade 12, Filters Fioroni, France), transferred quantitatively to 25 cm³ volumetric flasks and brought up to full volume with deionized water. Determining the phosphorus content in digested solutions was performed by using an Optima 2000 DV ICP-Optical Emission Spectrometer (PerkinElmer, Inc. Shelton, CT, USA). Analytical procedure scheme was presented in Fig. 1.

Results and discussion

The validation process leading to the determination of selectivity, linearity, limit of detection, limit of quantification, range, repeatability, intermediate precision, reproducibility and trueness has been described in this paper. The expanded uncertainty of sediment sample analysis with an ICP-OES technique also was estimated. All work was performed using two P lines: 213.617 nm and 214.914 nm (Tab. II).

Selectivity

Selectivity expresses the extent to which a particular method can be used to determine analytes under given conditions in the presence of other components in the sample (potential interferents impact to the analytical signal) [12]. To assess selectivity of the proposed method, the impact of potential interfering elements to the determination of phosphorus content was examined. For this purpose, standard solutions at three concentration levels: 1.0 mg dm⁻³, 10.0 mg dm⁻³ and 50.0 mg dm⁻³ were prepared by diluting a 1000 mg dm⁻³ ICP single-element standard solutions (Co, Cu, Fe, Mo, Zn, Al and Mg ICP standard solutions) then spiked with the phosphorus content equal to 1 mg dm⁻³ (see Reagents and calibration). The analysis of each prepared standard solution (with peak area measurement) was carried out in triplicate. The spectral analysis of signals (from characteristics wavelengths) showed the main interfering element was copper, overlapping on the phosphorus signal (Fig. 2). Based on the obtained results, recoveries of phosphorus were calculated. Low concentration of copper (1:1 P:Cu ratio) did not significantly affect on the phosphorus results, but high amount of this interferent (1:50 P:Cu ratio) made it impossible to determine phospho-

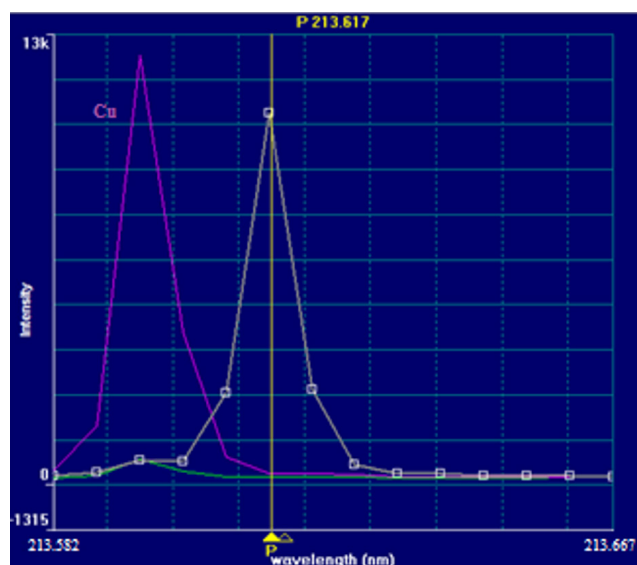


Fig. 2. Spectral overlap interference of Cu on P.

Tab. II. Validation parameters for developed method.

P wavelength, [nm]	213.617	214.914
Range of P content in standard solutions, [mg P dm ⁻³]	0.5-100	0.5-100
Linearity, r	>0.999	>0.999
LOD [mg P kg ⁻¹]	10	10
LOQ [mg P kg ⁻¹]	25	25
Repeatability, CV [%]	1.2	1.2
Intermediate precision, CV [%]	2.2	1.5
Trueness, R [%]	98.1	96.5
Expanded uncertainty, U (k=2), [%]	7.6	9.2

rus content accurately (Tab. III). The analysis was also performed with peak height measurement, then recoveries of phosphorus were calculated. This operation partially eliminated overlapping from copper (Tab. IV). Thus, determining phosphorus content in copper-rich samples, it is better to use the peak height as a processing mode.

Linearity

Linearity is defined as the ability to obtain test results directly proportional to the amount of analyte in the sample [13]. The linearity range is frequently determined by using calibration curves. In this research, the calibration was carried out as a function of spectrometer signal and phosphorus content. A series of proper concentrations of phosphorus in order to make the calibration curves was obtained by accurately prepared standard solutions at six concentration levels: 0.5 mg P dm⁻³; 2.0 mg P dm⁻³; 10.0 mg P dm⁻³; 20.0 mg P dm⁻³; 50.0 mg P dm⁻³ and 100.0 mg P dm⁻³ (see Reagents and calibration). Both calibration curves exhibited excellent a linear behavior ($r > 0.999$) in the entire measurement range for two P lines (Fig. 3).

Limit of Detection (LOD) and Quantification (LOQ)

Limit of detection (LOD) is the lowest concentration of analyte in a sample that can be detected but not necessarily quantitated as an exact value. However, limit of quantification (LOQ) is defined as the lowest concentration of analyte in a sample that can be quantitatively determined with suitable accuracy and precision [13]. LOD and LOQ were determined from analysis of blank samples and calculated to be a sum of mean values and standard deviation of them, multiplied by 3 and 10, respectively [14]. Assuming the sample mass of 0.5 g and the final volume of digested solution (25 cm³), LOD values were calculated at 10 mg P kg⁻¹, however LOQ values were equal to 25 mg P kg⁻¹ for both P lines.

Tab. III. Recoveries of phosphorus from mixed standard solutions (peak area).

P:Cu ratio	1:1	1:10	1:50
P 213.617 nm, R [%]	103	134	246
P 214.914 nm, R [%]	100	119	207

Tab. IV. Recoveries of phosphorus from mixed standard solutions (peak height).

P:Cu ratio	1:1	1:10	1:50
P 213.617 nm, R [%]	102	120	183
P 214.914 nm, R [%]	102	108	124

Range

The measurement range is defined as a concentration range from the LOQ value to the highest concentration of standard solution used for calibration [15]. In this research, it was therefore equal to 0.5-100 mg P dm⁻³. Assuming the mass of the sample at 0.5 g and the final volume of digested solution (25 cm³) the measurement range was corresponded to 25-5000 mg P kg⁻¹.

Precision

Precision is the closeness of degree of scatter between a series measurements obtained from multiple sampling of the same homogeneous sample under the prescribed conditions. Precision may be identified at three levels: repeatability, intermediate precision, and reproducibility. Each of these parameters is characterized by different measurement conditions [16, 17].

Repeatability

Repeatability express the precision under the same operating conditions over a short period of time (one laboratory, one analyst, the same instrument, standard solutions, and so forth) [17].

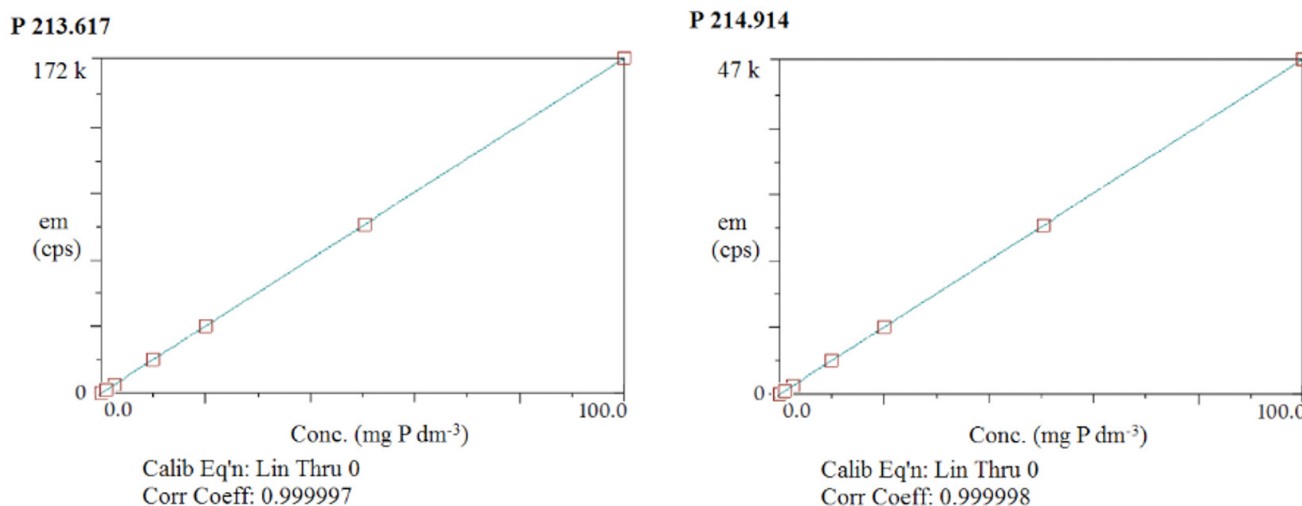


Fig. 3. Calibration curves as the functions of spectrometer signal (y) and phosphorus content (x).

In this study, repeatability was determined based on the results for samples of certified reference material (PACS-3) and it was calculated as an average coefficient of variation value for three series (each of ten independent determinations). Repeatability values were therefore equal to 1.2% for both P lines (Tab. II).

Intermediate precision

Intermediate precision characterizes variations within laboratories, such as different days, different analysts, different instruments, different standard solutions, etc. [18]. In this research, intermediate precision was expressed as a coefficient of variation value for a large series of results ($n=70$) for samples of PACS-3, carried out in six months. These values were calculated at 2.2% for P 213.617 nm and 1.5% for P 214.914 nm (Tab. II).

Reproducibility

Reproducibility expresses the precision between different laboratories. This level of precision is characterized by most variable measurement conditions (different laboratories with different equipment, analysts, time, etc.) [19]. The reproducibility value is usually given directly in reports from the interlaboratory comparison. In this study, reproducibility value calculated as a coefficient of variation for results from determining phosphorus content in sediment sample between twenty laboratories was equal to 10%.

Trueness

The accuracy is a closeness of agreement between the single measurement result and a reference value; however, trueness is defined as the closeness of agreement between an average value obtained from a large series of measurement results and a reference value [20]. In this research, trueness was determined based on the results ($n=70$) for samples of certified reference material (PACS-3). For this purpose, the obtained average value was compared with certified value. For both P lines the obtained average values were within the confidence interval of the manufacturer. Trueness was presented in the form of recovery values: 98.1% for P 213.617 nm and 96.5% for P 214.914 nm (Tab. II).

Uncertainty

According to the GUM [21], the definition of uncertainty of the measurement is: "a parameter, associated with the

result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand." The analytical uncertainty can be estimated by analyzing samples of certified reference material of the same amount and form of analyte and of the same matrix as the sample examined. In this study, the expanded uncertainty value of marine sediment sample analysis with an ICP-OES technique was estimated based on the results ($n=70$) for samples of certified reference material (PACS-3) carried out in six months. It was calculated in accordance with the following equation:

$$U = k \sqrt{u(Rw)^2 + \left(\sqrt{(\text{bias})^2 + \left(\frac{s_{CRM}}{\sqrt{n}} \right)^2 + u(Cref)^2} \right)^2}$$

where U is the expanded combined uncertainty close to 95% confidence interval; $u(Rw)$ is the standard uncertainty from intermediate precision; bias is the difference between mean measured value from a large series of test results and a certified value; s_{CRM} is the obtained standard deviation from measurements on the CRM; $u(Cref)$ is the uncertainty component from the certified value; k is the coverage factor. Finally, expanded uncertainty values of marine sediment sample analysis (on P content) with an ICP-OES technique were calculated at 7.6% for P 213.617 nm and 9.2% for P 214.914 nm (with a coverage factor of 2).

Summary and conclusions

Inductively coupled plasma-optical emission spectrometry is a good analytical tool for determining phosphorus content in marine sediment samples. A microwave-assisted aqua regia digestion provides a rapid, safe and efficient sample preparation. The method was characterized by high repeatability (coefficient of variation of 1.2%), trueness (recovery of 98.1%; 96.5%), and therefore high accuracy. The excellent linearity ($r > 0.999$) was observed in the entire measurement range (25-5000 mg P kg⁻¹). In highly contaminated samples, copper impact to the phosphorus results can be reduced by using the peak height as a processing mode. The low expanded uncertainty (7.6%; 9.2%) was associated with a high concentration of phosphorus in the marine sediment samples examined.

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