



Method validation for the determination of lead and arsenic emissions from stationary sources by inductively coupled plasma optical emission spectroscopy

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Abstract

Environmental pollution is currently one of the most pressing issues in Thailand, with air pollution being particularly concerning due to the prolonged presence of elevated contaminant levels that pose significant health risks. Monitoring air quality from stationary emission sources is crucial for assessing and controlling pollution to meet established standards. This research aims to validate a testing method and estimate the uncertainty in measuring the concentrations of Pb and As from stationary sources using ICP-OES. The findings indicate that the in-house method, based on U.S. EPA method 29, provides working range of 8.60 – 46.20 mg/m³ for Pb and 2.22 – 32.96 mg/m³ for As. In addition, the linearity and matrix effect tests for both heavy metals were within acceptable limits, with correlation coefficient not falling below 0.995 ($R = 0.9993$ for Pb and $R = 0.9991$ for As). Regarding matrix effects, the results showed that %difference of the slope remaining under 10%. Furthermore, the study reveals that the measurement uncertainty for Pb and As does not exceed 20% of the mid-to-high range.

Introduction

Air pollution is one of the most pressing environmental challenges, significantly impacting human health and the environment. Industrial emissions are among the major sources of air pollution, releasing pollutants such as particulate matter, gases, and heavy metals. Heavy metals, including lead (Pb) and arsenic (As), can accumulate in the environment and infiltrate the food chain, thereby increasing long-term health risks to humans. According to the Ministry of Industry of Thailand's standards for pollutant concentrations in factory emissions, it is specified that, in the case of no fuel combustion, the concentration of Pb must not exceed 30 mg/m³, and the concentration of As must not exceed 20 mg/m³. Similarly, in the case of fuel combustion, the concentration of Pb must not exceed 24 mg/m³, and the concentration of As must not exceed 16 mg/m³.⁽¹⁾

Objectives

1. To validate a testing method and assess the measurement uncertainty of Pb and As concentrations emitted from stationary pollution sources using ICP-OES.
2. To study the main parameter, including the limits of detection (LOD), limits of quantitation (LOQ), working range, matrix effects and uncertainty.

Method

The method for determining lead and arsenic concentrations in emissions from stationary sources, based on U.S. EPA Method 29⁽²⁾, begins with isokinetic sampling. This process involves capturing particulate matter using heated filters and absorbing gases in a solution containing 10% hydrogen peroxide and 5% nitric acid. The collected samples are then digested by microwave digestion to determine Pb and As in the samples using ICP-OES, as shown in Figure 1.

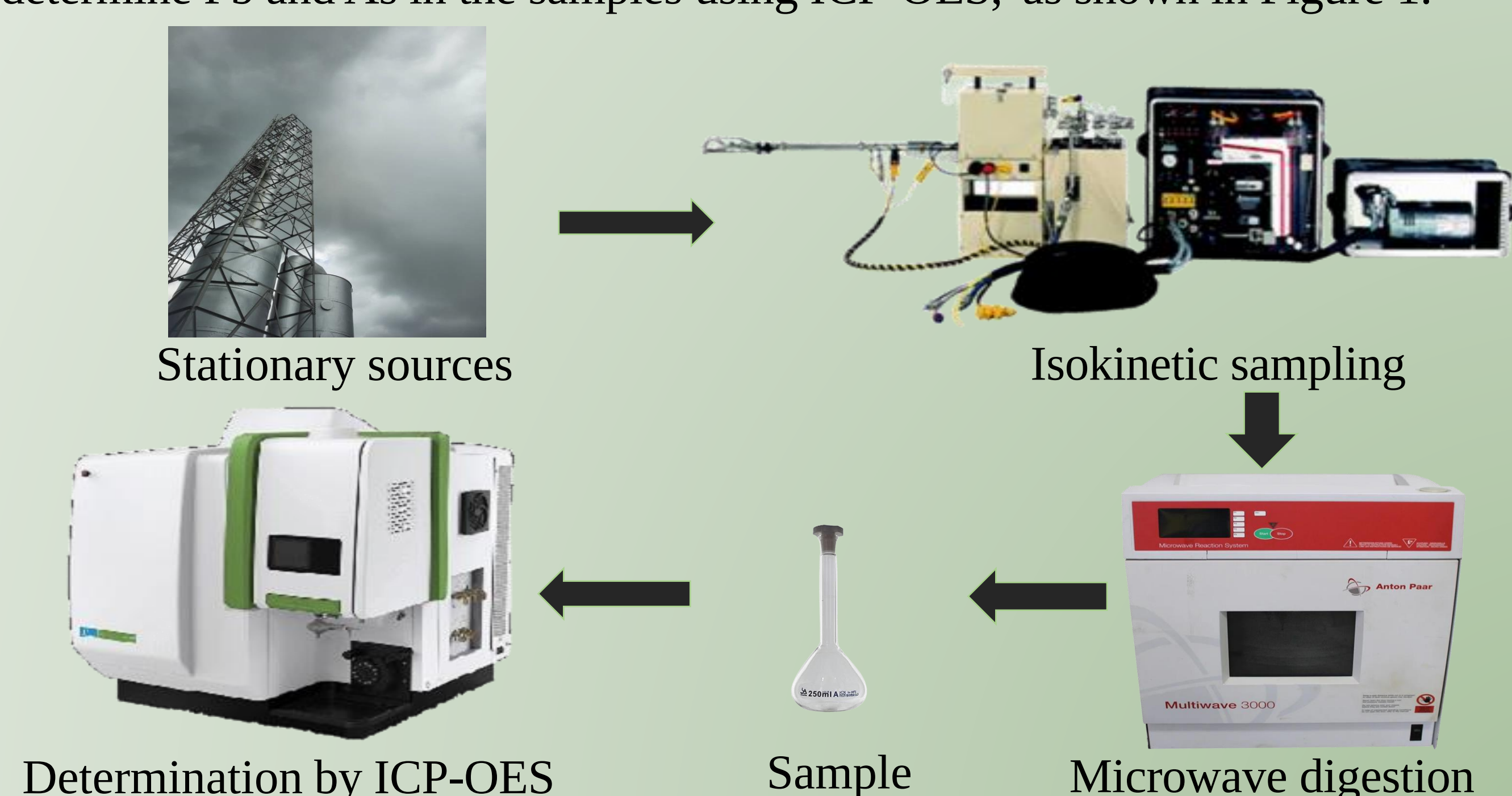


Figure 1. The method for sample determination

Results and Discussion

1. LOD and LOQ

The calculated LOD values for Pb and As were 2.37 mg/m³ and 0.17 mg/m³, respectively. Similarly, the LOQ values for Pb and As were 7.91 mg/m³ and 0.57 mg/m³, respectively.

2. Working range

The spiking sample was prepared at three concentrations (low, medium, and high), with the low concentration selected based on LOQ values. The range of an analytical procedure refers to the interval between the lower and upper concentration of an analyte in the sample for which the procedure demonstrates an acceptable level of linearity, accuracy, and precision.

Results and Discussion

Table 1. Linearity results for the proposed method

Linearity results	Pb	As
Instrument working range (mg/L)	0.1–10	0.1–10
Linear equation	$y = 15901x - 217.93$	$y = 4350.4x - 188.76$
Coefficient of determination (R^2)	0.9987	0.9983
Correlation coefficient (R)	0.9993	0.9991

Table 1 confirms the linearity, with acceptance criteria set at $R^2 > 0.990$ or $R > 0.995$. The medium and high concentrations were diluted to fit within the standard curve. The concentrations of Pb and As were analyzed in mg/L using ICP-OES. Moreover, the standard air volume (m³) used in the sampling procedure was used to calculate the Pb and As concentrations in mg/m³. The working ranges for Pb (8.60 – 46.20 mg/m³) and As (2.22 – 32.96 mg/m³) are shown in Table 2.

Table 2. Results of the working range evaluation at three concentrations

Analyte	Sample + Spikes (mg)	Values of spiked (mg)	Conc. in air (mg/m ³)	%Recovery ^a	%RSD ^b
Pb	Sample + 8	7.69	8.60	96.17	7.41
	Sample + 20	20.78	23.35	103.89	5.65
	Sample + 40	41.09	46.20	102.72	2.32
As	Sample + 2	1.98	2.22	98.95	3.58
	Sample + 10	11.00	12.36	97.87	0.42
	Sample + 30	29.33	32.96	97.78	1.42

^a The accepted range is 80 – 110%, ^b The accepted is less than 10%

3. Matrix Effect

Matrix effects were evaluated by comparing the slopes of standard and spiked samples. The %difference values were 4.17% for Pb and 2.28% for As, both well within the acceptance limit of less than 10%.

4. Uncertainty

The combined uncertainty was calculated at a 95% confidence level. The uncertainty for Pb is 42.1%, 12.5%, 6.0% at three concentrations (low, medium and high, respectively). Similarly, the uncertainty for As is 27.6%, 6.2%, 4.9% at three concentrations (low, medium and high, respectively).

Conclusion

The validation of a method for determining Pb and As of emissions from stationary sources using ICP-OES demonstrated satisfactory results. This study successfully determined the concentrations of Pb and As with ICP-OES, achieving acceptable accuracy and precision in mid-to-high concentration ranges. However, high uncertainty was observed at low concentrations, primarily due to matrix effects and limitations in instrument sensitivity. Future research should focus on implementing pre-concentration techniques, improving sample preparation protocols, and employing more sensitive instruments to address these challenges.

References

1. Ministry of Thailand. <https://www.diw.go.th/webdiw/wp-content/uploads/2021/07/law-fac-env-31102549.pdf> (Accessed December 2024.)
2. U.S. EPA Method 29. <https://www.ecfr.gov/current/title-40/chapter-I/subchapter-C/part-60/appendix-Appendix%20A-8%20to%20Part%2060> (Accessed December 2024.)

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