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Mathematical equation correction to spectral and transport interferences in high-resolution continuum source flame atomic absorption spectrometry: determination of lead in phosphoric acid

Abstract: Divalent metal complexes of ligand 2-methoxybenzylidenepyruvate with Fe, Co, Ni, Cu and Zn as well as sodium salt were synthesized and investigated in the solid state. TG curves of these compounds were obtained with masses sample of 1 and 5mg under nitrogen atmosphere. Different heating rates were used to characterize and study these compounds from the kinetic point of view. The activation energy and pre-exponential factor were obtained applying the Wall-Flynn-Ozawa method to the TG curves. The obtained data were evaluated and the values of activation energy (E_a / kJ mol^{-1}) was plotted in function of the conversion degree (α). The results show that due to mass sample, different activation energies were obtained. The results are discussed mainly taking into account the linear dependence between the activation energy and the pre exponential factor, where was verified the effect of kinetic compensation (KCE) and possible linear relations between the dehydrations steps of these compounds.

Keywords: bivalent metal ions, 2-methoxybenzylidenepyruvate, non-isothermal kinetics, dehydration

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[3,4]. However both main and secondary lines for Pb are interfered if variations in phosphoric acid concentrations occur, changing the aspiration rate of the nebulizer.

Correction of spectroscopy interferences by mathematical equations in inductively coupled plasma mass spectrometry (ICP-MS) technique has already been established [5,6]. Nevertheless the adaptation of such mathematical equations to atomic absorption spectrometry for spectral interference correction was not feasible due to the lack of a truly simultaneous multi-element system. Recently and upon the introduction of a high-resolution continuum source atomic absorption spectrometry (HR-CS AAS) [7], this problem has been overcome as the whole spectral environment around the analytical line can be acquired [8,9]. Using this technique, the interference caused by PO molecules at the main line for Pb at 217.0005 nm may be eliminated using the least-squares background correction (LSBC) [1]. The alternate line at 283.3060 nm is unaffected by PO, but both main and secondary lines are interfered by transport effects. A method using the LSBC plus internal standardization was recently proposed to minimize these interferences in the determination of Pb in phosphoric acid by HR-CS FAAS [1].

In this paper, a new approach to overcome spectral and transport interferences associated with the determination of Pb in phosphoric acid by HR-CS FAAS has been proposed. In principle, spectral overlap can be corrected providing that another wavelength of the interfering element is itself free from interference. The feasibility of using mathematical equation correction previously employed in ICP-MS, to eliminate spectral interference caused by PO molecules at the 217.0005 nm Pb line and transport interference caused by variations in phosphoric acid concentrations in the determination of Pb in phosphoric acid has been investigated.

Materials and methods

Instrumentation

All measurements were carried out using an Analytik Jena ContrAA 300 high-resolution continuum source flame atomic absorption spectrometer equipped with a xenon short-arc lamp XBO 301 [10] with a nominal power of 300 W operating in a hot-spot mode as a continuum radiation source. This new equipment presents a compact high-resolution double-Echelle grating monochromator correspondent to a spectral band width < 2 pm per pixel in the far ultraviolet range and a charge-coupled device (CCD) array detector.

High-purity (99.7%) acetylene (Air Liquid, Brazil) was used as fuel gas. Air-acetylene oxidizing flame was used for analyte atomization. Solutions were directly aspirated by the burner / nebulizer system of the spectrometer using an injection module (SFS 6) enabling the computer-controlled aspiration of blanks, analytical solutions and samples.

Reagents, analytical solutions and samples

High purity de-ionized water (resistivity 18.2 MΩ cm) obtained using a Millipore Rios 5® reverse osmosis and a Millipore Milli-Q Academic® deionizer system (Bedford, MA, USA), and Merck Suprapur® nitric acid (Darmstadt, Germany) were used throughout to prepare all solutions. All chemical reagents used were of analytical grade.

Reference solutions containing 0.10, 0.20, 0.40, 0.80 and 1.00 mg L^{-1} Pb were daily prepared by appropriate dilution of the 1000 mg L^{-1} single stock standard solutions (Normex ™, Carlo Erba, Italy) and acidified to 1% (v/v) with HNO$_3$.

Working standard solutions containing 1.0, 2.5, 5.0 and 7.5% (m/v) H$_3$PO$_4$ were prepared by dissolving 1.18, 2.48, 5.88 and 8.82 g of analytical reagent grade phosphoric acid 85% (Mallinckrodt, Xalostoc, Mexico) in 1% (v/v) solution. Blank solution was prepared containing only HNO3 in 1% (v/v).

Additionally, it should be stressed that the line for PO at 217.0458 nm is within the spectral window for Pb at 217.0005 nm (Figure 1). The ratio between slopes of curves for PO (slope $^{217.0005\ nm}$/slope $^{217.0458\ nm}$) was calculated daily taking into consideration that changes in the operating parameters alter the measured absorbance. However, ratios obtained in different days were usually within 1.23 – 1.29, but were not significantly different at the 95% confidence level (paired *t-test*).
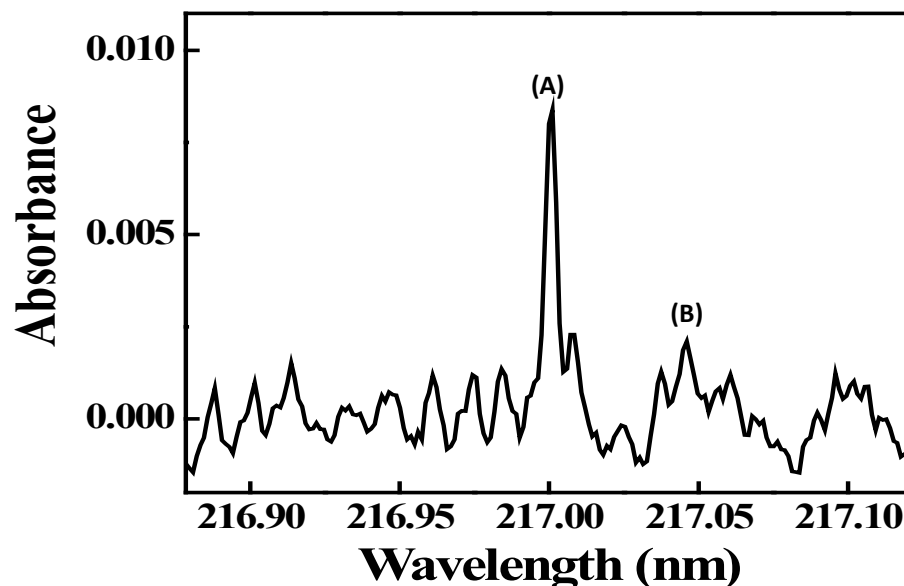

Figure 1. Spectrum recording for spiked Pb in phosphoric acid. (A) and (B) correspond to lines at 217.0005 nm and 217.0458 nm, respectively.

Analysis of test solutions and samples

The feasibility of the mathematical correction for spectral and transport interferences was verified in the determination of Pb in test solutions and two phosphoric acid samples (Table 1). Results for samples were in agreement at a 95% confidence level (paired *t-test*) with those obtained by HR-CS FAAS using LSBC plus internal standardization. Precision and accuracy studies were also carried out using test solutions, or else, recovery experiments for diluted [1% – 7.5% (m/v)] phosphoric acid samples spiked with 100 and 400 μg L^{-1} Pb.

If no correction method is applied, the concentrations of Pb found were in the 140 – 230 μg L^{-1} and 420 – 480 μg L^{-1} intervals for spiked samples with 100 and 400 μg L^{-1} Pb, respectively. These results showed severe spectral interference caused by PO affected measurements at 217.0005 nm causing a positive interference much more pronounced than the interference caused by the transport effect. On the other hand, when the mathematical equation approach was employed, the found concentrations of Pb were close to Pb spikes (recoveries in the 97.5 – 100% range), suggesting the usefulness of the proposal to eliminate spectral and transport interference. Relative standard deviations of measurements varied from 1.4 to 4.3% and 2.0 to 6.0% (n = 12) without and

Resumo: Um método de correção de interferência espectral e de transporte é proposto, e foi aplicado para minimizar interferências por moléculas de PO produzidas em chama ar-acetileno e de transporte causada pela variação da concentração de ácido fosfórico. Átomos de Pb e moléculas de PO absorvem a 217,0005 nm, então $A_{total}^{217,0005\ nm} = A_{Pb}^{217,0005\ nm} + A_{PO}^{217,0005\ nm}$. Monitorando o comprimento de onda alternativo de PO em 217,0458 nm, é possível calcular a contribuição relativa de PO na absorbância total a 217,0005 nm: $A_{Pb}^{217,0005\ nm} = A_{total}^{217,0005\ nm} - A_{PO}^{217,0005\ nm} = A_{total}^{217,0005\ nm} - k\ (A_{PO}^{217,0458\ nm})$. O fator de correção k é a razão entre os coeficientes angulares de duas curvas analíticas para P obtidas a 217,0005 e 217,0458 nm ($k = b^{217,0005\ nm}/b^{217,0458\ nm}$). Fixando-se a taxa de aspiração da amostra em 5,0 ml min^{-1}, e integrando-se a absorbância no comprimento de onda a 3 *pixels*, curvas analíticas para Pb (0,1 - 1,0 mg L^{-1}) foram obtidas com coeficientes de correlação típicos $\geq 0,9990$. As correlações lineares entre absorbância e concentração de P nos comprimentos de onda 217,0005 e 217,0458 foram $\geq 0,998$. O limite de detecção de Pb foi 10 µg L^{-1}. O método de correção proposto forneceu desvios padrão relativos ($n=12$) de 2,0 a 6,0%, ligeiramente menores que os obtidos sem correção (1,4-4,3%). As recuperações de Pb adicionado às amostras de ácido fosfórico variaram de 97,5 a 100% (com correção pelo método proposto) e de 105 a 230% (sem correção).

Palavras-chave: método de correção por equação matemática; espectrometria de absorção atômica com fonte contínua e de alta resolução; chumbo; ácido fosfórico.

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