



Simultaneous Determination of Pb(II), Cu(II) and Ni(II) with MEDTA by Ultraviolet and Visible Derivative Spectrophotometry

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Authors' contributions

This work was carried out in collaboration between all authors. Author MCFF designed the study, wrote the protocol, performed the statistical analysis, managed the literature searches and wrote the first draft of the manuscript. Authors JMCR and JMFS managed the analyses of the study. All authors read and approved the final manuscript.

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ABSTRACT

Aims: Since the end of the nineteenth century, when Werner proposed his theory of co-ordination, the study of metallic compounds has continued to attract the interest of researchers. The present work had as its aim to achieve simultaneous determination of Pb(II), Cu(II) and Ni(II) by means of UV-VIS and derivative spectrophotometry, using methyl-ethylene-diamine-tetraacetic acid, MEDTA, as a chelating agent.

Study Design: The visible and ultraviolet spectroscopy allows both to identify a chemical substance (qualitative analysis) and to determine its concentration (quantitative analysis). In the work, the UV-VIS and derivative spectrophotometry is used for the determination simultaneous of Pb(II), Cu (II) and Ni (II). The method proposed uses methyl-ethylene-diamine-tetracetic acid (MEDTA) as a chelating agent and absorption spectrophotometry for quantification.

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Place and Duration of Study: The study is part of a doctoral thesis, was conducted in the Analytical Chemistry Department of the University of A Coruña.

Methodology and Results: In the range of wavelengths between 200 nm and 500 nm, the complexes formed by MEDTA with Pb(II) or Cu(II) present a single absorption peak at 256 nm and 272 nm respectively, whilst the complex formed with Ni(II) presents two peaks at 250 nm and 380 nm. In the samples in which the three elements are present, the spectrum shows two peaks: the first at 260 nm, due to the superposition of the individual absorption peaks of the cations at 250, 256 and 272 nm and the second at 380 nm, characteristic of Ni (II). It is necessary the joint use of the normal or direct spectrum (zero order) and the first derivative thereof by means of the zero-crossing-point method for its simultaneous determination.

In the development of this method the influences exercised by pH, time and temperature were determined. The reproducibility of the method proposed was checked, as was the interference from certain of the more frequent anions and cations that might affect the determination.

Conclusion: As long as the optimum conditions indicated are maintained, the method of analysis proposed makes possible the simultaneous determination of Pb(II), Cu(II) and Ni(II) using MEDTA as a chelating agent and UV-VIS and derived spectrophotometry. Then method was successfully tested through the use of blind samples.

Keywords: Derivative spectrophotometry; zero crossing point; lead; copper; nickel; MEDTA.

1. INTRODUCTION

Since the end of the nineteenth century, when Werner proposed his theory of coordination, the study of metallic compounds has continued to attract the interest of researchers.

Among the range of chelating agents one group (the complexones) stands out, being characterized by having in their molecules α -amino acids to whose nitrogen atom is additionally linked a methyl-carboxylic group, which with many metallic cations gives rise to internal complexes, in general soluble and very stable. Of all these acids the most important and widely known is ethylene-diamine-tetracetic acid, EDTA. Methyl-ethylene-diamine-tetracetic acid (MEDTA) is also included within this family, being a chelating agent analogous to EDTA, but with the difference that it has an asymmetric carbon bound to a methyl radical. This acid was synthesized by Dwyer and Garvan [1] and its use as a chelating agent has been extensively studied.

Almost all of the applications of polyamino-carboxylate sequestering agents are based on their fundamental property of forming very stable and soluble complexes with the majority of metallic ions. The stability of these complexes depends on $[H]^+$ and $[OH]^-$, on the solubility products of the possible co-existent salts, on the ionic strength of the solution and whether the cation is found in isolation or in the presence of

others capable of becoming a part of the complex. Polyamino-carboxylate compounds have one great advantage when being used as masking agents, the fact that the complexes are in general formed almost instantaneously and in stoichiometric proportions. Another advantage is their action as chromogenic agents.

Since "cation-complexone" complexes present well-formed characteristic bands in the ultraviolet-visible (UV-VIS) range of the spectrum, these polyamino-carboxylate agents can be used in simple, rapid, routine and relatively cheap analytic methods for the spectrophotometric determination of metallic cations. Most of the properties of these complexes are determined by the nature of the organic chelating agent that combines with the metallic ion. The properties of the metallic ions in the complex are changed, so that they do not show their normal behaviour in response to reagents. Once they have entered into a complex they can no longer be discovered through precipitation, being sequestered or masked.

Absorption spectrophotometry has often been used in the study of complexes formed by a metallic cation and an organic ligand [2]. The advantage is that it can be applied to a wide range of concentrations, often with just a simple calibration curve. It may also be used successfully in simultaneous determinations of metallic cations if the spectrum produced does not have overlapping absorption peaks.

Table 1. Cation-MEDTA complexes

Cation	Interval	λ nm	pH	Calibration Line	R^2	$\mu\text{g/ml}$
Pb(II)		256	6.0	$[A]_{256} = 6.30 \cdot 10^{-3} [\text{Pb(II)}] + 0,1789$	0.997	50-400
Cu (II)	200 – 500	272	9.0	$[A]_{272} = 4.66 \cdot 10^{-2} [\text{Cu(II)}] - 0,0903$	0.998	10-45
Ni (II)	nm	250	3.0	$[A]_{250} = 5.15 \cdot 10^{-4} [\text{Ni(II)}] + 0,1294$	0.993	494-1482
		380		$[A]_{380} = 2.03 \cdot 10^{-4} [\text{Ni(II)}] - 0,0082$	0.996	

Fernández-Feal [3] studied the absorption spectra of the complexes formed by Pb(II), Cu(II) and Ni(II) with MEDTA in order to determine the wavelengths at which the absorption peaks corresponding to each of these elements occur and the fulfilment of Beer's Law. Determination coefficients, R^2 , greater than 0.990 were obtained, as is shown in Table 1.

If there is an overlap between individual absorption peaks in the zero-order spectrum of samples in which two or more cations are present, derived spectrophotometry can be brought into play to resolve them [4,5,6]. Derived spectrophotometry represents a relatively recent analytic aspect of spectroscopy, even though it was first introduced somewhat more than fifty years ago.

Until the principle of electronic differentiation was introduced, this technique was limited to obtaining the first derivative, which restricted its applications. O'Haver et al. have undertaken an excellent study of the theoretical aspects of this technique and its multiple potential uses [7,8,9].

In the quantitative analysis of mixtures with two or more components by means of derived spectrophotometry, successful use can be made of the zero crossing point method [10,11,12,13,14]. This is based on the fact that, at the wavelength at which the maximum absorption of one component occurs in the zero-order spectrum, there is a cancelling out of $dA/d\lambda$ in the first-order spectrum (first derivative). Hence, the value of the first derivative at this wavelength depends exclusively upon the concentration of the second component.

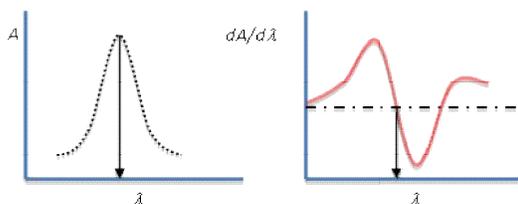


Fig. 1. Normal absorption spectrum (zero order) and its first derivative (first order)

A number of studies of the simultaneous determination of cations by means of derived spectrophotometry, involving the pairs formed by Pb(II) and Cu(II), Pb(II) and Ni(II) and Cu(II) and Ni(II), using MEDTA as a chelating agent, have validated the zero crossing point method for the quantification of these cations when more than one of them is present in the samples and the peaks on the direct spectrum overlap [3,15].

The determination of Pb(II), Cu(II) and Ni(II) [16,17] has aroused interest among researchers, since these cations are present simultaneously in a wide range of real samples. It has been undertaken with a number of different techniques and on very varied matrices, by means of ICP (Inductively Coupled Plasma) and GFAAS (Graphite Furnace Atomic Absorption Spectrometry) in edible oils [18] and in alloys by means of ETAAS (Electrothermal Atomic Absorption Spectrometry) [19].

2. MATERIALS AND METHODS

2.1 Equipment

- SHIMADZU-160 UV-VIS spectrophotometer equipped with a microprocessor, optical recorder and copier. It can produce derivatives from the first to the fourth with a $\Delta\lambda$ running from 0.6 to 72.0 nm, and a range of absorbance from -2.500 to +2.500 \pm 0.002. It uses prismatic quartz cells with a 1 cm light passage.
- CRISON-2000 pHmeter.

2.2 Reagents

- 5% MEDTA solution.
- Sodium hydroxide, 0.1 M and 1.0 M aqueous solutions.
- Hydrochloric acid, 0.1 M and 1.0 M aqueous solutions.
- Lead(II), $4.83 \cdot 10^{-3}$ M target pattern solution, prepared from a Merck Titrisol solution of trioxonitrate(V) of lead(II) in water, volumetrically assessed with EDTA using

eriochrome black T as an indicator and tartrate to prevent precipitation of the lead.

- Copper(II), $1.57 \cdot 10^{-3}$ M target pattern solution, prepared from a Merck Titrisol solution of copper(II) chloride in water, volumetrically assessed with EDTA using eriochrome-T black as an indicator.
- Nickel(II), $8.42 \cdot 10^{-2}$ M target pattern solution, prepared from hexahydrated nickel(II) chloride, assessed with EDTA using murexide as an indicator.

2.3 Method

2.3.1 Basis of the method

When the absorption spectrum of a Pb(II)/Cu(II)/Ni(II)/MEDTA mixture between 200 nm and 500 nm is studied, a peak characteristic of the Ni(II)/MEDTA complex is observed at 380 nm, whilst at 260 nm the peaks corresponding to the absorption of each of the three cations in this

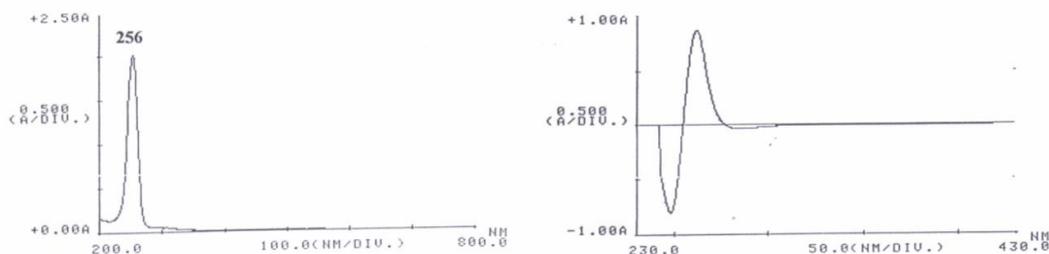


Fig. 2. Zero-Order spectrum and first derivative for the Pb(II)/MEDTA complex

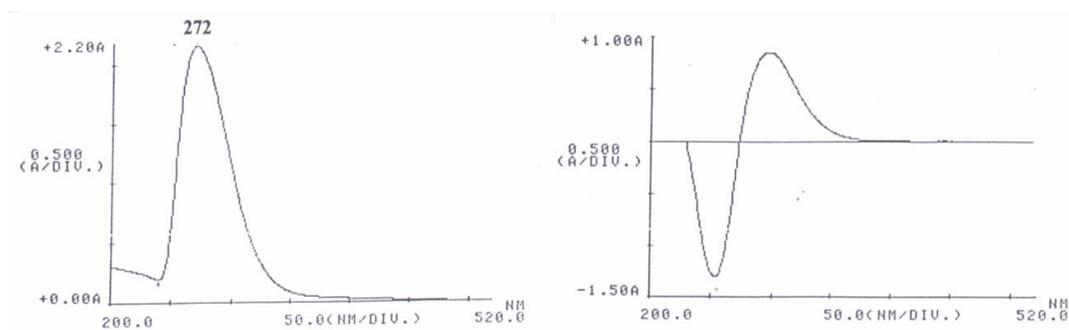


Fig. 3. Zero-Order spectrum and first derivative for the Cu (II)/MEDTA complex

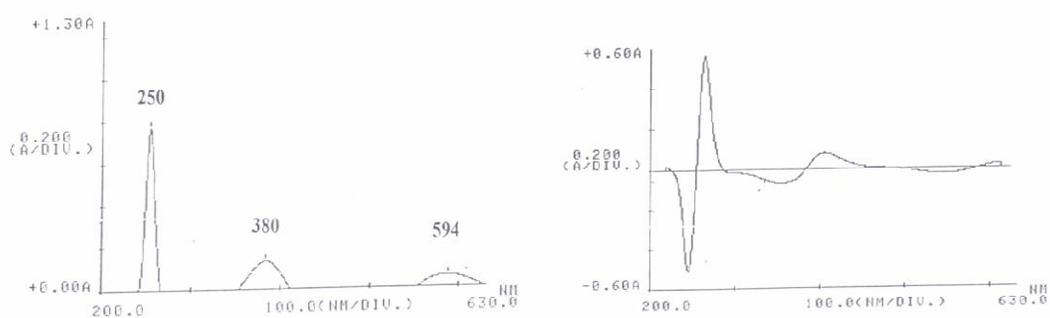


Fig. 4. Zero-Order spectrum and first derivative for the Ni (II)/MEDTA complex

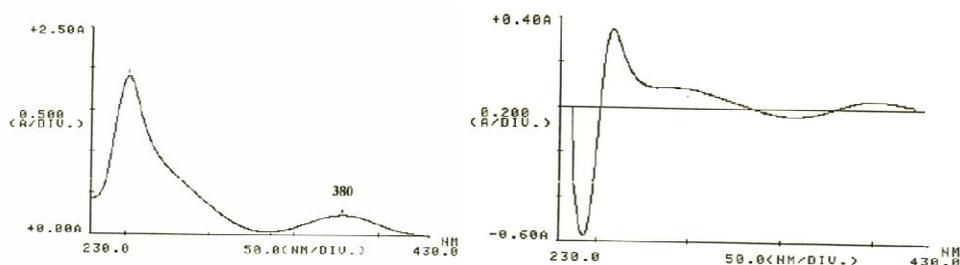


Fig. 5. Zero-Order spectrum and first derivative for the Pb(II)/Cu(II)/Ni(II)/MEDTA complex

zone of the spectrum (250 nm, 256 nm and 272 nm) overlap and appear as a single peak. To resolve this last peak, use is made of the first derivative of the absorption spectrum, this being a geometrical point on the slope of the spectrum in absorbance units per nm of wavelength that measures the variation in absorbance against the wavelength (dA/dλ). The derived spectrum follows the same relationship with concentration as does the normal (zero-order) spectrum. This means that it fulfils Beer's Law if the latter does.

2.3.2 Method proposed

The sample is dissolved, and an aliquot of it is put into a 10 mL graduated flask, 3 mL of 5% MEDTA are added, the pH is adjusted to 3.0 and the final volume is made up with Milli-Q water. The zero-order absorption spectrum of the sample is obtained, as is its first derivative with a $\Delta\lambda$ of 20 nm, and compared with a target prepared under the same conditions as the sample, over a range from 200 nm to 500 nm.

The value measured in the zero-order spectrum for absorbance at 387 nm allows the quantification of Ni(II) in the sample. To determine the concentrations of Pb(II) and Cu(II), the measurements for dA/dλ in the first derivative of the spectrum at 272 nm and 256 nm, expressed in arbitrary units, are used, respectively.

For the determination of the concentrations of Pb(II), Cu(II) and Ni(II) it is necessary first to establish the calibration lines corresponding to these cations with target pattern solutions of known concentration.

3. RESULTS AND DISCUSSION

The validity of the method for the simultaneous determination of Pb(II), Cu(II) and Ni(II) was demonstrated in several types of sample. The

first type had a Pb(II) content of between 100 µg/mL and 273 µg/mL in the presence of 20 µg/mL of Cu(II) and 1.482 µg/mL of Ni(II). The second involved samples with a Cu(II) content of between 10 µg/mL and 30 µg/mL in the presence of 100 µg/mL of Pb(II) and 1.482 µg/mL of Ni(II). The third type had samples with a Ni(II) content of between 988 µg/mL and 1.976 µg/mL in the presence of 100 µg/mL of Pb(II) and 20 µg/mL of Cu(II).

3.1 Selection of Optimum Analytic Parameters

3.1.1 Influence of pH

A series of solutions was prepared by putting into 10 mL graduated flasks aliquots of target pattern solution of Pb(II), Cu(II) and Ni(II), with a wide range of concentrations, 3 mL of 5% MEDTA and drops of 0.1 M HCl solution and/or 0.1 M NaOH so as to cover the largest possible range of pH values. Milli-Q water was used to make these up to the desired final volume.

The zero-order absorption spectrum and its first derivative were obtained for each solution between 200 nm and 500 nm. In the direct spectrum the figure for absorbance at 380 nm was determined, while in the derived spectrum the values corresponding to dA/dλ at 250 nm, 256 nm, 272 nm and 380 nm were determined in arbitrary units, against a target prepared in analogous conditions to the samples studied.

The results demonstrated that the figures for the parameters $dA/d\lambda_{256\text{nm}}$ and $dA/d\lambda_{272\text{nm}}$, coming from the first derivative of the absorption spectrum, and the values for absorbance at 380 nm, $A_{380\text{nm}}$, obtained from the zero-order spectrum, remained constant over a pH range between 2.0 and 5.0. In addition, it is of considerable relevance that in this pH range, at the wavelengths where the absorption peaks

corresponding to nickel (II) lie in the wavelength range studied, the zeroing of $dA/d\lambda$ occurs in the first derivative of the spectrum. This is crucial in establishing the validity of the first derivative for quantifying the other two cations present.

3.1.2 Influence of time and temperature

Twenty-five solutions with a known concentration of Pb(II), Cu(II) and Ni(II) were prepared under the conditions described in the method proposal. Five of these solutions were kept at ambient temperature, whilst the other twenty were heated for 1, 3, 5, 7 and 10 minutes at 40°C, 60°C, 80°C and 100°C, then allowed to cool down to ambient temperature before the zero-order absorption spectrum and its first derivative were produced.

Consideration of the figures obtained for A_{380nm} and $dA/d\lambda$ at 250 nm, 256 nm, 272 nm and 380 nm permits the conclusion that temperature and heating time do not influence the stability of the system at ambient temperature. However, if the temperature rises above 60°C, the system ceases to remain stable.

Consideration of the influence exercised by time over the stability of the system allows it to be concluded that the formation of chelates is instantaneous and the system that is formed is stable for a long period of time.

3.1.3 Calibration lines

Three batches, each composed of five samples, were prepared. In these, the concentration two of the cations under study was kept constant while the third was varied in order to find the equation allowing quantification of the concentration of each of them in the presence of the other two. For this purpose, the requisite volume of each of the standard solutions of Pb(II), Cu(II) and Ni(II) of known concentration was put into 10 mL graduated flasks, 3 mL of 5% MEDTA were added, the pH was adjusted to 3.0 and Milli-Q water was used to make the quantity up to the required final volume. Thereafter, the zero-order

absorption spectrum was produced, as was its first derivative, over a range from 200 nm to 500 nm with a $\Delta\lambda$ of 12 nm, using being made as a reference of a target prepared under the same conditions as the samples.

In each series of samples the figure for absorbance at 380 nm was determined on the direct spectrum, while the derived spectrum was used to find the values for $dA/d\lambda$ at 250 nm, 256 nm, 272 nm and 380 nm. From the figures obtained in this way, the calibration lines permitting the simultaneous quantification of Pb(II), Cu(II) and Ni(II) over the range of concentrations studied were determined.

In the Table 2 is shown the calibration lines and determination coefficients for the quantification of each of the cations present in samples over the Range of Concentrations Considered. These were obtained from the first derivative of the spectrum in the case of Pb(II) and Cu(II) and from the direct spectrum in the case of Ni(II).

3.1.4 Interference

The possible interferences that any frequently present cations and anions might cause in determinations were investigated. The results obtained indicate that with regard to cations interference was noted once a concentration of 100 $\mu\text{g/mL}$ was reached in the case of aluminium(III), manganese(II), magnesium(II) and zinc(II). For bismuth(III), cerium(III), iron(III), chrome(III) and cobalt(II) the relevant concentration was 10 $\mu\text{g/mL}$, whilst a concentration of 1 $\mu\text{g/mL}$ applied to selenium(IV) and vanadium(IV).

In respect of anions, the presence of fluoride, carbonate, oxalate, acetate, tetraborate, tungstate, nitrite and molybdate interfered with the first derivative of the absorption spectrum of mixtures of complexes once their concentration rose to 100 $\mu\text{g/mL}$. Thiosulphate and phosphate, for their part, had this effect once a concentration of 10 $\mu\text{g/mL}$ was reached.

Table 2. Calibration lines and determination coefficients for the quantification of each of the cations present in samples

Samples containing simultaneously Pb(II), Cu(II) y Ni(II)						
Cation	λ nm (A)	λ nm (dA/d λ)	pH	Calibration Line	R ²	$\mu\text{g/ml}$
Pb (II)	256	272	3.0	$[dA/d\lambda]_{272} = 2.831 \cdot 10^{-4} [Pb(II)] + 0,0886$	0.996	100-300
Cu (II)	272	256		$[dA/d\lambda]_{256} = 0.0145 [Cu(II)] + 0,1392$	0.995	10-30
Ni (II)	380	-		$[A]_{380} = 1.785 \cdot 10^{-4} [Ni(II)] + 0,0058$	0.994	988-1976

Table 3. Concentrations stated and detected by application of the method proposed

$\mu\text{g/mL}$	SAMPLE N°1		SAMPLE N°2	
	Stated	Detected	Stated	Detected
Pb(II)	100.0	104.2 \pm 3.4	200.0	196.7 \pm 4.5
Cu(II)	10.0	10.0 \pm 0.1	20.0	20.1 \pm 0.1
Ni(II)	988.0	990.1 \pm 4.5	988.0	986.7 \pm 4.0

3.2 Application

In order to verify the validity of the method, it was applied to two blind samples containing varying quantities of Pb(II), Cu(II) and Ni(II) and other cations in concentrations that did not interfere in later spectrophotometric determination by the method of analysis proposed:

SAMPLE N°1: 100 mg/mL Pb(II) - 10 $\mu\text{g/mL}$ Cu(II) - 988 $\mu\text{g/mL}$ Ni(II) - 200 $\mu\text{g/mL}$ Ca(II) - 122 $\mu\text{g/mL}$ Mg(II)

SAMPLE N°2: 200 $\mu\text{g/mL}$ Pb(II) - 20 $\mu\text{g/mL}$ Cu(II) - 988 $\mu\text{g/mL}$ Ni(II) - 343 $\mu\text{g/mL}$ Ba(II) - 281 $\mu\text{g/mL}$ Cd(II)

The results obtained were compared with those expected from the method initially proposed. This demonstrated its validity for the range over which the concentrations of the cations investigated, the value for absorbance measured on the direct spectrum at 380 nm and the figures for $dA/d\lambda$ taken from the derived spectrum in arbitrary units at 256 nm and 272 nm presented a linear correlation.

4. CONCLUSION

As long as the optimum conditions indicated are maintained, the method of analysis proposed makes possible the simultaneous determination of Pb(II), Cu(II) and Ni(II) using MEDTA as a chelating agent and UV-VIS and derived spectrophotometry, fundamentally as an outcome of the following facts:

1. Between 200 nm and 500 nm, the direct spectrum presents two absorption peaks, the second of which, at 380 nm, is due exclusively to the presence of Ni(II). The figure for absorbance at this wavelength, once the relationship $A_{380\text{nm}}/\text{Ni(II)}$ is known, permits determination of the concentration of this cation in the sample.
2. Consideration of the first derivative of the spectrum by the zero crossing point method allows it to be seen that $dA/d\lambda_{250\text{nm}}$ cancels

out, so that the value corresponding to $dA/d\lambda_{256\text{nm}}$ is linked solely to the presence of Cu(II) and the figure for $dA/d\lambda_{272\text{nm}}$ exclusively to the presence of Pb(II). Once the corresponding calibration lines are known, these last two figures permit the quantification of these cations in the sample.

The method was successfully used with blind samples. It can be applied to the determination of Pb(II), Cu(II) and Ni(II) in samples of contaminated soils.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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