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Interferences from titanium and zirconium during calcium determination by flame spectrometry

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Abstract: Titration methods based on an inhibition effect were used to investigate the interferences from Ti and Zr in the determination of Ca by atomic absorption and flame emission spectrometry using an air–acetylene flame. Changes either in the absorption or emission signal of Ca were continuously registered on a computer display and characteristic titration curves were obtained. The mole ratios between Ti or Zr and Ca at characteristic points on titration curves were used to explain the quantitative changes occurring in the solution being titrated and aspirated into the flame. In order to investigate procedures for eliminating these interferences, a method of atomic absorption inhibition release titration was used. For this purpose, a solution of La, as a releasing agent with a very low Ca concentration, used as an indicator, was continuously titrated with the solution of Ti as inhibitor. A comparative study of the activity of Ba, Sr and La as releasing agents was investigated during titration of Ca with Zr solution. Based on the calculated mole ratios between Zr and Ba, Sr or La, the effectiveness of these agents in eliminating the interferences was determined. Possible reactions occurring during evaporation of the aerosol in the air–acetylene flame are represented by chemical equations.

Keywords: interference, calcium determination, titanium and zirconium, flame atomic absorption and emission spectrometry, titration method, releasing action.

INTRODUCTION

Interferences causing lower results during calcium determination by atomic absorption (emission) flame spectrometry in the presence of Ti or Zr have been reported in the literature.[1] Titanium and zirconium, being the inhibiting agents during the flame spectrometric determination of Ca, are assumed to form thermostable products with this alkaline earth metal.[2] This so-called inhibition effect is especially evident in low-temperature flames.[3]

In this study, titration based on the inhibition effect[4] was used to investigate

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the interferences from Ti or Zr during the determination of calcium in an air–acetylene flame. Definite volumes of standard solutions of titanium or zirconium (titrand solution) were continuously titrated against a standard solution of $CaCl_2$ and *vice versa*. Simultaneously, as the titrand solution was aspirated into an air–acetylene flame, changes in absorption or emission of the Ca signal (422.7 nm) were monitored on a computer display. Titration curves with distinct characteristic points were obtained. The mole ratios between the inhibitors (Ti or Zr) and calcium at these inflection points were used to explain the processes occurring during evaporation of the aerosol in the flame.

It is important to note that the term "titration" is used here to designate an operation, *i.e.*, a procedure employed for the study of processes occurring in a flame, rather than to its conventional sense in volumetric analysis.

Interferences from Ti or Zr during the determination of calcium are commonly eliminated by addition of La.[5] Also, Sr or Ba can be used to eliminate chemical interferences during calcium determination.[6,7]

The continuous titration method, termed atomic absorption inhibition release titration[8] was employed in a study of the elimination of interferences from Ti and Zr during the determination of Ca. For this purpose, a solution of La with a very low concentration of Ca, as an indicator, was continuously titrated with Ti. Changes in the atomic absorption signal of the indicator (Ca) were automatically recorded and titration curves with distinct inflection points compared to the blank curves were obtained. The determined mole ratios between Ti and La were used to explain the releasing action of La. The activity of Ba, Sr and La in the elimination of interferences was investigated during titration with a Zr solution, in the presence of Ca as indicator. Based on calculated mole ratios between Zr and corresponding releasing agents, their effectiveness in the elimination of interferences was determined. Possible reactions occurring during evaporation of an aerosol in an air–acetylene flame are presented by chemical equations.

The aim of this study was to summarize the quantitative results obtained in a study of reactions occurring between Ti and Ca or Zr and Ca, and thus advance our understanding of the changes in equilibrium occurring during the evaporation of an aerosol in an air–acetylene flame. Also, the releasing action of La in the elimination of interferences by Ti during the determination of Ca was studied. An investigation of the effectiveness of Ba, Sr and La in eliminating interferences from Zr has a scientific rationale, as well as an economic one, because the market prices of Ba, Sr or La salts vary significantly.

EXPERIMENTAL

Instrumentation and chemicals

A SpectrAA 220 Varian atomic absorption (emission) flame spectrometer was used for all the titration measurements. The spectrometer was attached to computer which enabled the automatic monitoring of changes either in the absorption or emission of the Ca signal. During the titration, the titrand solution was stirred with a magnetic stirrer and a beaker with the titrant solution was connected to a peristaltic pump (LKB Bromma). The titrant solution was added at constant flow rate (about 3 ml min^{-1}) from a microburette through a tap connected by a capillary to the peristaltic pump. The rate of titrant addition was approximately equal to the rate of titrand aspiration into the flame, in order to minimize changes in volume during the titration.

Continual titration measurements were performed in an air–acetylene flame, with a 0.7 cm burner height, following the procedure described previously.[9,10] Changes in emission of Ca (at 422.7 nm) occurring during titration were followed using a 0.2 nm slit width. Changes in the calcium atomic absorption (at 422.7 nm) were followed employing a hollow cathode lamp (Varian) for Ca, operating at 10.0 mA.

Highly purified, deionized water used for the preparation of all dilute standard solutions, was obtained using an Elga PURELAB Option-R 7/15 water purification unit. Standard Ca, Ba and Sr solutions were prepared by dissolving previously dried appropriate carbonates (*p.a*. Merck and *p.a*. Carlo Erba, Milano) in the minimal volume of 2M HCl or HNO_3. The La(III) solution was prepared from lanthanum chloride heptahydrate ($LaCl_3 \cdot 7H_2O$, *p.a*. 98 % BDH laboratory reagents, England).

Standard solutions of Ti and Zr were prepared by dissolving$TiCl_4$ (Baker, USA), *i.e*., $Zr(NO_3)_4$ (*p.a*. Merck). The concentrations of Ti and Zr in these solutions were determined gravimetrically *via* the corresponding dioxides, using the cupferron method.[11]

RESULTS AND DISCUSSION

The study of the interferences from titanium

In order to study the interferences from titanium, a $TiCl_4$ solution, in the 10–50 μg Ti ml^{-1} concentration range, was titrated with a $CaCl_2$ solution in which the calcium concentration was 500 μg ml^{-1}. The titration curves in this case had a characteristic shape with a significant inflection domain labelled by point a (Fig. 1).

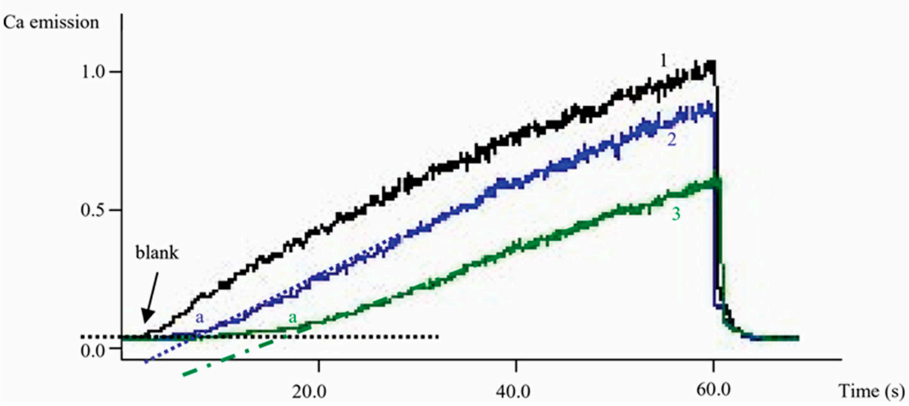

Fig. 1. Titration of 50 ml water (1), 10 μg Ti ml^{-1} (2) and 50 μg Ti ml^{-1} (3) with $CaCl_2$ standard solution (500 μg Ca ml^{-1}).

At the beginning of titration, the Ca emission at 422.7 nm changed only slightly, *i.e*., Ti exerted a considerable depressive effect on the calcium emission. This occurs because Ti reacts with Ca and thermostable products are simultaneously formed during the evaporation of the aerosol. Further addition of the titrant (500 μg Ca ml^{-1}) leads to a rapid increase in the emission signal, which enables the graphical determination of the titration end-point a. In order to calculate mole ratios Ti/Ca at point a, it is nessecary to subtract the volume of $CaCl_2$ added during the titration of 50 ml deionized water, the so-called blank volume (Fig. 1, curve 1).

Calculation of mole ratios between Ti and Ca at the characteristic point a (Table I) showed them to be variable. Namely, mole ratios Ti/Ca increase with increasing concentration of Ti in titrand solution, which indicates the occurrence of an equilibrium change during the formation of thermostable mixed oxides, *i.e.*, $CaO\cdot 5TiO_2$ and $CaO\cdot 6TiO_2$:

$$Ti/Ca = 5.2 \;\Rightarrow\; CaCl_2 + 5TiCl_4 + 11H_2O \rightarrow CaO\cdot 5TiO_2 + 22HCl$$

$$Ti/Ca = 6.1 \;\Rightarrow\; CaCl_2 + 6TiCl_4 + 13H_2O \rightarrow CaO\cdot 6TiO_2 + 26HCl$$

TABLE I. Mole ratios Ti/Ca obtained by titration of $TiCl_4$ solution with $CaCl_2$ solution (500 μg Ca ml^{-1})

Ti concentration / μg ml^{-1}	Mole ratios Ti/Ca at the inflection point a of the titration curves
10	3.5
20	4.3
30	5.2[a]
40	6.1
50	6.2

[a] The relative standard deviation (RSD) value for five replicates is 7.0 %.

The formation of these mixed oxides with variable contents of CaO and TiO_2, which are introduced into flame as aerosol particles, indicates strongly the possible reactions occurring in the air–acetylene flame (disregarding possible influences of the combustion of the flame gases). Hence, the interference observed during Ti titration with $CaCl_2$ solution, can be ascribed to the much slower evaporation of the obtained calcium titanates, with respect to $CaCl_2$.[12]

When a reverse titration was performed, *i.e.*, when a solution of $CaCl_2$ was titrated with a titanium solution, the flame emission of Ca at the beginning of titration increased rapidly, depending on the calcium concentration in the titrand solution (Fig. 2). After a brief period, the Ca emission sharply decreased, which enables the determination of the so-called threshold of sensitivity of the indicator present – emission at 422.7 nm (point a).

On further addition of $TiCl_4$, the emission decreased gradually (depending on the Ti concentration in the titrant solution), because of the formation of new stoichiometric compounds between Ca and Ti, which enables the determination of the titration end-point b. The mole ratios Ti/Ca at points a and b were calculated and are presented in Table II.

In contrast, in the case of the titration of Ti with calcium solution, the mole ratios between Ti and Ca decreased with increasing calcium concentration (as titrand), which indicates that the formed thermostable mixed oxides have a higher CaO content.[13,14] It was observed that the Ti/Ca values (at point b) increased with increasing concentration of Ti as titrant when the Ca concentration was constant, which proves that the composition of the mixed oxides depends on both the titrand and titrant concentration. The calculated mole ratios at the first point (a) designate the threshold of the Ca flame emission signal and it was registered that Ti inhibited Ca even when its concentration in the solution was ten times lower than Ca concentration (Table II, Ti/Ca = 0.1).

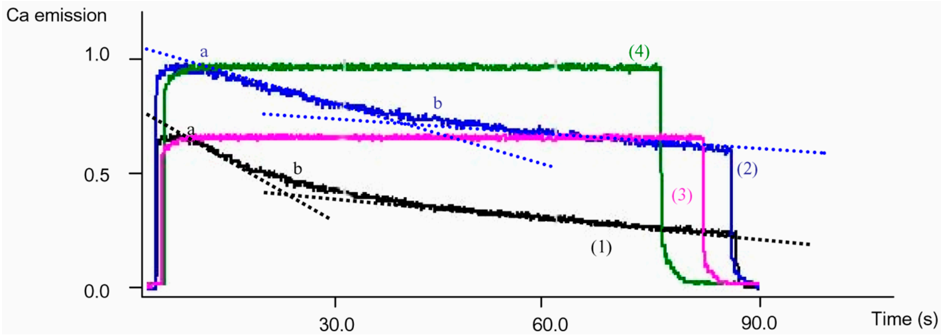

Fig. 2. Titration of 10 µg Ca ml^{-1} (1) and 20 µg Ca ml^{-1} (2) with $TiCl_4$ standard solution (500 µg Ti ml^{-1}) and aspiration of 10 µg Ca ml^{-1} (3) and 20 µg Ca ml^{-1} (4) as blank curves.

TABLE II. Mole ratios Ti/Ca obtained by titration of a $CaCl_2$ solution with a $TiCl_4$ solution

Ca concentration / µg ml^{-1}	Mole ratios Ti/Ca at the inflection points of the titration curves					
	Titrant concentration / µg Ti ml^{-1}					
	200		400		500	
	a	b	a	b	a	b
5	0.1	1.0	0.2	1.2	0.2	1.5
10	0.1^{A}	0.7^{B}	0.2^{C}	0.9^{D}	0.1^{E}	1.0^{F}
15	0.1	0.6	0.1	0.7	0.1	0.9
20	0.1	0.5	0.1	0.7	0.1	0.7

RSD values for five replicates are: ^{A}0.4, ^{B}2.1, ^{C}0.8, ^{D}4.6, ^{E}2.2 and ^{F}4.5 %.

It should be mentioned that similar results were obtained during the monitoring of the Ca absorption signal at 422.7 nm. Also, mole ratios Ti/Ca remained almost the same when the titrations of Ti with Ca, and *vice versa*, were performed by monitoring the emission signal at 622.0 nm (CaO band).

The study of interferences from zirconium

The processes occurring during Zr titration with a calcium chloride solution are described by the titration curves shown in Fig. 3. In contrast to the titration of $TiCl_4$, the titration curves in this case show a sharp increase in the calcium absorption signal, rather than a gradual one. The existence of two distinct inflection points, a and b, on the titration curves clearly indicates that inhibition was present, but it is less intensive in comparison to Ti as the inhibitor.

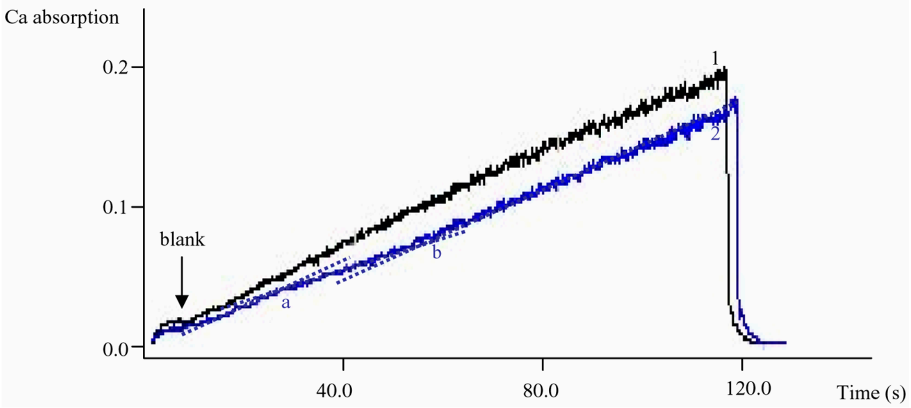

Fig. 3. Titration of 50 ml water (1) and 8 μg Zr ml^{-1} (2) with $CaCl_2$ standard solution (100 μg Ca ml^{-1}).

The mean values of the mole ratios Zr/Ca calculated at point a (Table III) indicate the possible formation of a mixed sesquioxide between Ca and Zr during the evaporation of the aerosol (irrespective of whether the absorption, *i.e.*, emission, at 422.7 nm or emission at 622.0 nm was measured):

$$Zr/Ca = 1.4 \Rightarrow 2CaCl_2 + 3Zr(NO_3)_4 + 2H_2O \rightarrow 2CaO{\cdot}3ZrO_2 + 4HCl + 12NO_2 + 3O_2$$

TABLE III. Mole ratios Zr/Ca obtained by titration of a $Zr(NO_3)_4$ solution with a $CaCl_2$ or $Ca(NO_3)_2$ solution (100 μg Ca ml^{-1})

Zr concentration / μg ml^{-1}	Mole ratios Zr/Ca at the inflection points of the titration curves			
	Titrant			
	$CaCl_2$		$Ca(NO_3)_2$	
	a	b	a	b
8	1.6	1.0	1.7^A	1.0
10	1.4^B	1.0^C	1.3^D	0.9^E
12	1.4	0.9	1.6	0.9
15	1.3^A	0.9	1.4	1.0
18	1.4	0.7^A	1.4	0.9
Mean values	1.4^F	1.0^G	1.4^H	0.9^I

^{A}These values are not taken into account.

RSD values for five replicates and the mean values are: 10.4^B, 4.2^C, 8.7^D, 5.3^E, 8.7^F, 5.0^G, 10.9^H and 4.9^I %.

Undoubtedly, at the second inflection point, b, the mean stoichiometric ratios (Table III) show that calcium metazirconate – $CaO{\cdot}ZrO_2$ was formed (melting point 2550 °C).[15] The possible reaction occurring between Ca and Zr in the evaporating aerosol can be presented as follows:

$$Zr/Ca = 1.0 \Rightarrow CaCl_2 + Zr(NO_3)_4 + H_2O \rightarrow CaO{\cdot}ZrO_2 + 2HCl + 4NO_2 + O_2$$

In the case of Ca titration with $Zr(NO_3)_4$ solution, the titration curves have three pronounced inflection points (Fig. 4). The first one (point a) enables the determination of the earlier-mentioned threshold of the indicator sensitivity, *i.e.*, Ca emission (422.7 nm) in the presence of the inhibitor Zr, and it is very similar to the one obtained by titration with titanium.

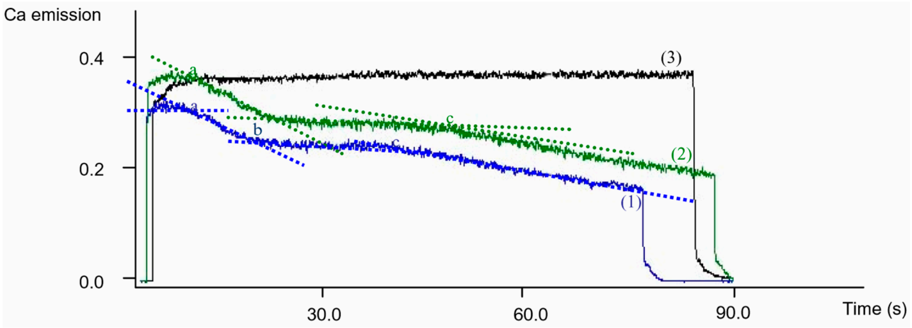

Fig. 4. Titration of 4 μg Ca ml^{-1} (1) and 5 μg Ca ml^{-1} (2) with $Zr(NO_3)_4$ standard solution (400 μg Zr ml^{-1}) and aspiration of 5 μg Ca ml^{-1} (3) as blank curve.

The mean mole ratios within the respective points b and c are obviously very similar, regardless of the changing titrand (Ca) or titrant (Zr) concentrations (Table IV).

TABLE IV. Mole ratios Zr/Ca obtained by titration of a $CaCl_2$ solution with a $Zr(NO_3)_4$ solution

Ca concentration / μg ml^{-1}	Mole ratios Ti/Ca at the inflection points of the titration curves					
	Concentration / μg Zr ml^{-1}					
	300			400		
	a	b	c	a	b	c
4	0.1	0.7	1.5	0.2	0.7	1.5
5	0.2^{A}	0.6^{B}	1.4^{C}	0.2^{D}	$0.6^{E, F}$	1.4^{G}
8	0.2	0.7	1.5	0.2	0.7	1.6
10	0.2	0.7	1.5	0.2	0.6	1.6
12	0.2	0.6	1.5	0.2	0.6	1.4
15	0.2	0.6	1.4	0.2	0.7	1.3^{H}
Mean values	0.2^{I}	0.6^{J}	1.5^{K}	0.2^{L}	$0.6^{M, N}$	1.5^{O}

RSD values for five replicates and mean values are: 1.7^{A}, 2.6^{B}, 6.9^{C}, 1.6^{D}, 1.9^{E}, 6.2^{G}, 3.7^{I}, 5.0^{J}, 4.7^{K}, 0^{L}, 5.0^{M} and 8.9^{O} %.
^{H}This value was not taken into account.
The 95 % confidence limits for the titration end-point and mean values are: $(0.65 \pm 0.02)^{F}$ and $(0.6 \pm 0.1)^{N}$.

On the basis of the mean mole ratios of Zr/Ca, obtained at inflection points b and c, it can be concluded that mixed sesquioxides: $2CaO{\cdot}3ZrO_2$ and $3CaO{\cdot}2ZrO_2$ are formed in air–acetylene flame through the following possible reactions (disregarding possible influences of the combustion of the flame gases):

$$Zr/Ca = 0.6 \Rightarrow 3CaCl_2 + 2Zr(NO_3)_4 + 3H_2O \rightarrow 3CaO{\cdot}2ZrO_2 + 6HCl + 8NO_2 + 2O_2$$

$$Zr/Ca = 1.5 \Rightarrow 2CaCl_2 + 3Zr(NO_3)_4 + 2H_2O \rightarrow 2CaO{\cdot}3ZrO_2 + 4HCl + 12NO_2 + 3O_2$$

As was mentioned earlier concerning the formation of Ca titanates, the depression of the absorption (or emission) signal of Ca in the presence of Zr can be explained in the same manner. Namely, in this case, the interference effect of Zr must be attributable to the slower volatilization of the formed thermostable calcium zirconates.[15]

A study of releasing action of some common reagents in eliminating interferences from Ti and Zr

In order to investigate the releasing action of La in eliminating interferences from Ti, a lanthanum chloride solution (in the presence of 4 µg Ca ml^{-1} as indicator) was titrated with a $TiCl_4$ solution containing 400 µg Ti ml^{-1}, whereby the Ca absorption at 422.7 nm was followed. The obtained titration curves are characterized by an inflection point a (Fig. 5). The absorption of Ca evidently increased at first and then, during the reaction of La with Ti, it remained nearly constant (until the inflection point a was attained). Thereafter, with further addition of titanium, the absorption of Ca commences to decrease, due to the reaction of Ca as indicator.

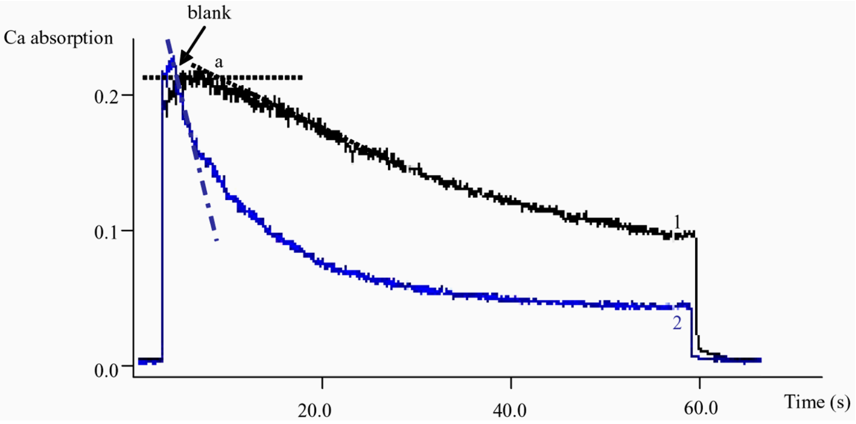

Fig. 5. Titration of 20 µg La ml^{-1} in presence of 4 µg Ca ml^{-1} (1) and 4 µg Ca ml^{-1} as a blank (2) with $TiCl_4$ standard solution (400 µg Ti ml^{-1}).

The mole ratios Ti/La can be determined at point a by subtracting the blank volume, which refers to the titration of 4 µg Ca ml^{-1} without La, with the same concentration of Ti, as inhibitor (Fig. 5, curve 2). The mole ratios between Ti and La at point a remained nearly constant, which suggests that a thermostable compound is formed between lanthanum and titanium – $La_2O_3 \cdot TiO_2$ (Table V).

The effectiveness of Ba, Sr and La as releasing agents was investigated during titration with Zr solution as inhibitor. For this purpose, standard solutions of Ba, Sr or La with 2 µg Ca ml^{-1} (as indicator) were titrated with 500 µg Zr ml^{-1}. The changes in the Ca absorption were continuously registered and at the characteristic inflection points, mole ratios of Zr and the releasing agent were determined (Table VI).

It is evident from the mean mole ratios shown in Table VI that Zr reacts with barium approximately in a 1:3, with strontium in a 1:1, and with lanthanum in a

1:2 ratio. Based on these quantitative data, the releasing agents may be sequenced as: Sr > La > Ba regarding their effectiveness in eliminating the interference of Zr during the determination of Ca. This is because 97.3 g Sr, 277.8 g La and as much as 457.8 g Ba, are required to eliminate the interference from about 91.2 g Zr in the form of $Zr(NO_3)_4$.

TABLE V. Mole ratios Ti/La obtained by titration of lanthanum chloride in the presence of 4 μg Ca ml^{-1} (as indicator) with a $TiCl_4$ solution (400 μg Ti ml^{-1})

La concentration / μg ml^{-1}	Mole ratios Ti/La
5	0.5
10	0.6
15	0.5
20	0.5[a]
25	0.6

[a]RSD value for five replicates is 3.4 %.

TABLE VI. Mole ratios Zr/Ba, Zr/Sr and Zr/La obtained by the titration of the corresponding releasing agents in presence of 2 μg Ca ml^{-1} (as indicator) with a $Zr(NO_3)_4$ solution (500 μg Zr ml^{-1})

Ba, Sr, La Concentration / μg ml^{-1}	Mole ratios Zr/Ba	Mole ratios Zr/Sr	Mole ratios Zr/La
10	0.3	1.0[a]	0.6
20	0.3	0.9	0.5
25	0.4	0.9	0.5
30	0.3[b]	0.8	0.5[c]
Mean values	0.3[d]	0.9[e]	0.5[f]

RSD values for five replicates and mean values are: 3.2[a], 0.8[b] and 1.4[c], 4.3[d], 7.1[e] and 4.3[f] %.

According to the calculated mean mole ratio values presented in Table VI, the reactions between the releasing elements (Ba, Sr or La) and Zr most probably occurring during evaporation of the aerosol in an air–acetylene flame, disregarding the effects of combustion of the flame gases, can be expressed as follows:

$$Zr/Ba = 0.3 \Rightarrow 3BaCl_2 + Zr(NO_3)_4 + 3H_2O \rightarrow 3BaO{\cdot}ZrO_2 + 6HCl + 4NO_2 + O_2$$

$$Zr/Sr = 0.9 \Rightarrow SrCl_2 + Zr(NO_3)_4 + H_2O \rightarrow SrO{\cdot}ZrO_2 + 2HCl + 4NO_2 + O_2$$

$$Zr/La = 0.5 \Rightarrow 2LaCl_3 + Zr(NO_3)_4 + 3H_2O \rightarrow La_2O_3{\cdot}ZrO_2 + 6HCl + 4NO_2 + O_2$$

CONCLUSIONS

Titration methods based on an inhibition effect were used for the study of the interferences from Ti and Zr during Ca determination by flame spectrometry in air–acetylene flame. Titration curves of a characteristic shape with distinct inflection points were obtained. The mole ratios Ti/Ca or Zr/Ca at these points were used to explain the processes occurring during evaporation of the aerosol in the flame. It may be concluded that variable thermostable mixed oxides xCaO·yTiO$_2$ are formed during the determination of Ca in the presence of Ti. The values of the x and y coefficients vary, depending on the concentration of the element being titrated (titrand) or the concentration of the element in the titrant solution. Unlike Ti, during Ca determination in the presence of Zr, it seems that thermostable mixed oxides with a constant composition are formed, such as $3CaO\cdot 2ZrO_2$, $2CaO\cdot 3ZrO_2$ and $CaO\cdot ZrO_2$. The formation of these oxides probably occurs due to a much higher melting point of zirconates.

Elimination of the interference of Ti during the determination of Ca with La as the releasing agent was examined using the continuous atomic absorption inhibition release titration method. Releasing action of La occurs through reactions based on a change of the equilibrium in the evaporating aerosol, which results in the formation of thermostable mixed oxide $La_2O_3\cdot TiO_2$. The different releasing actions of Ba, Sr and La were investigated during calcium titration with $Zr(NO_3)_4$. It can be concluded that Zr reacts with Ba at an approximately 1:3, with Sr at 1:1 and with La at 1:2 mole ratio. These quantitative data suggest the following sequence series: Sr > La > Ba, considering the releasing action in the elimination of the interference of Zr. This parameter is important both in scientific and economic terms.

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ИЗВОД

СМЕТЊЕ ОД ТИТАНА И ЦИРКОНИЈУМА ПРИ ОДРЕЂИВАЊУ КАЛЦИЈУМА ПЛАМЕНОМ СПЕКТРОМЕТРИЈОМ

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У овом раду су за проучавање сметњи од титана и цирконијума, при одређивању калцијума атомском апсорпционом и емисионом пламеном спектрометријом, разрађене методе титрације, које се базирају на ефекту инхибиције. У том циљу одређене запремине раствора инхибитора, Ti или Zr, континуално су титроване раствором калцијума и обрнуто, уз симултано распршивање титранда у ваздух–ацетиленски пламен. Истовремено, праћене су промене у апсорпцији, односно емисији калцијума на дисплеју рачунара. На овај начин су добијене титрационе криве са израженим превојним тачкама, у којима су израчунати молски односи између инхибитора (титана, односно цирконијума) и калцијума. Добијени молски односи су искоришћени за објашњење квантитативних промена до којих долази у току испаравања капи раствора у пламену. Упоредна проучавања поступака за елиминисање сметњи од Ti и Zr су вршена методом атомске апсорпционе "ослобађајуће" инхибиторске титрације. У том циљу, раствори "ослобађајућих" реагенаса (баријума, стронцијума или лантана) су титровани раствором цирконијума уз регистровање промена у апсорпцији Ca, као индикатора. Утврђено је да La уклања сметње од Ti и Zr при одређивању калцијума, реагујући са Ti и Zr у молском односу 1:2, при чему Ca остаје "слободан". На исти начин, доказано је да Ba и Sr реагују са Zr у различитим односима, у току спектрометријског одређивања Ca. На бази израчунатих молских односа између цирконијума и баријума, односно стронцијума или лантана, утврђено је да се одговарајући "ослобађајући" реагенси, према ефикасности у сузбијању сметњи, могу сврстати у низ: Sr > La > Ba, што је значајно како са научног, тако и са економског становишта.

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