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Conductometric method for the quantitative analysis of Pb(II) and Cd(II) with 2-mercapto-5-*R*-amino-1, 3, 4-thiadiazole derivatives[1]

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Abstract

The reactions of the cations with 2-mercapto-5-*R*-amino-1,3,4-thiadiazole derivatives were studied conductometrically with the purpose of establishing a new conductometric method for the quantitative analysis of Pb(II) and Cd(II). Aqueous solutions of $Pb(NO_3)_2$ and $Cd(CH_3COO)_2$ were titrated with hidroalcoholic solutions of 2-mercapto-5-amino-1,3,4-thiadiazole (MATD), 2-mercapto-5-allylamino-1,3,4-thiadiazole (MAlATD) and 2-mercapto-5-acetylamino-1,3,4-thiadiazole (MAcATD) and 2-mercapto-5-phenilamino-1,3,4-thiadiazole (MFATD) in different concentrations. The reactions takes place at pH 6.5 (realised with acetate buffer). A linear classical titration curves was obtained. In solutions more concentrated than 10^{-2} M just one equivalence point can be noticed, corresponding to 1:2 Me:R stoechiometries. For concentration less than 10^{-2} M two equivalence point were observed at 1:1 and 2:1 ratio of Me:R, indicating the step formation of the complex. Accurate conductometric determinations can be made using the second break points of the titration curves as equivalence points. The amounts of Cd(II) and Pb(II) taken and recovered are good, with an error less than 1%.

Keywords: Conductometric method; 2-Mercapto-1,3,4-thiadiazole; Tetracon 96; Titrations curves

1. Introduction

The conductibility determinations are largely used for studying the chemical reactions and the properties of complex combinations and of hardly soluble compounds. It is also used in quantitative determinations, taking into account the fact that conductometric titrations can be applied to all kinds of reactions (acido–basic, precipitation, redox, complexing reactions).

Previous research within the Analytical Chemistry Department of the Faculty of Pharmacy of Cluj-Napoca concerning the 2-mercapto-5-*R*-

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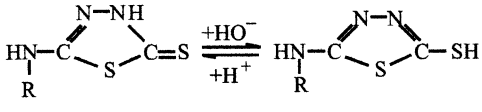
amino-1,3,4-thiadiazole derivatives (cyclization products of bisthioureea bisubstituted derivatives) which were used for the quantitative determination of heavy metal cations, showed that Pb^{2+}, Cd^{2+}, Cu^{2+}, Hg^{2+} form with these reagents hardly soluble combinations, which are stable, coloured and can be analytically studied. Thus, a new scheme for separating the cations has been proposed [1], there were elaborated new methods for gravimetric analysis [2–4] and also a method for preconcentration traces of various cations with 2-MFATD impregnated on silica gel [5].

This present study is a result of our studies on the reactions of 1,3,4-thiadiazole derivatives aiming at finding other possibilities for their analytical use. This paper proposes to analyse the formation process of hardly soluble combinations also by means of conductometric titration based upon the precipitation reaction. This study enabled us to elaborate a new conductometric method for the quantitative analysis of cations.

Then have been studied the reactions leading to precipitate of Pb^{2+} and Cd^{2+} with four the 2-mercapto-5-*R*-amino-1,3,4-thiadiazole derivatives:



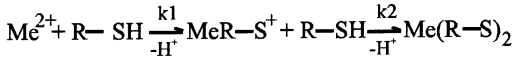
R=H; 2-mercapto-5-amino-1,3,4-thiadiazole (MATD)

R=alyl; 2-mercapto-5-alylamino-1,3,4-thiadiazole (MAlATD)

R=acetyl; 2-mercapto-acetylamino-1,3,4-thiadiazole (MAcATD)

R=phenil; 2-mercapto-5-phenilamino-1,3,4-thiadiazole (MFATD)

The general reaction is:



soluble insoluble

Pb^{2+} and Cd^{2+} form with these reagents in neuter or in a slightly acid solution (pH 6.5 realised with 0.1 M CH_3COONa) crystalline precipitates which are yellow and white, respectively. The composition of the precipitate obtained was established by elementary chemical analysis, which are also confirmed by the potentiometric, spectrophotometric and gravimetric methods [3,6].

2. Materials and methods

We used 10^{-2} M-10^{-4} M $Pb(NO_3)_2$ and $Cd(CH_3COO)_2$ solutions from which were titrated fixed volumes with 2-mercapto-5-*R*-amino-1,3,4-thiadiazole derivatives having concentrations ranging from 10^{-2} to 10^{-4} M. In order to prepare the solutions of cations were used Merck reagents (p.a.) and the titre was established complexonometrically by Na_2EDTA titration in the presence of indicators: xilenolorange (for Pb^{2+}) and T erioblack (for Cd^{2+}).

The solutions of the organic reagents used were prepared with 70% etilic alcohol and their titre was established by accurate weighing in a volumetric flask (pure reagents were used) and then it was checked up by potentiometric titration with 0.1 M NaOH.

The determinations were performed at the room temperature, under continuous agitation. The conductivity values were registrated at a fixed time interval 60 s after adding the titrating solution. Conductometric titrations were performed by microprocessor conductivity meter LF 537 with Tetracon 96 graphite electrode. In order to compare the results, under the same circumstances, determinations were also performed with a RK 102 Radelkis conductometer (with Pt platinated electrodes) as well as with a conductivity cell with silver spiral and stainless steel electrodes (elaborated at the Faculty of Chemistry of Cluj-Napoca) [7].

The curves of conductometric titration of Pb^{2+} with MATD using cells with different electrodes are given in Fig. 1.

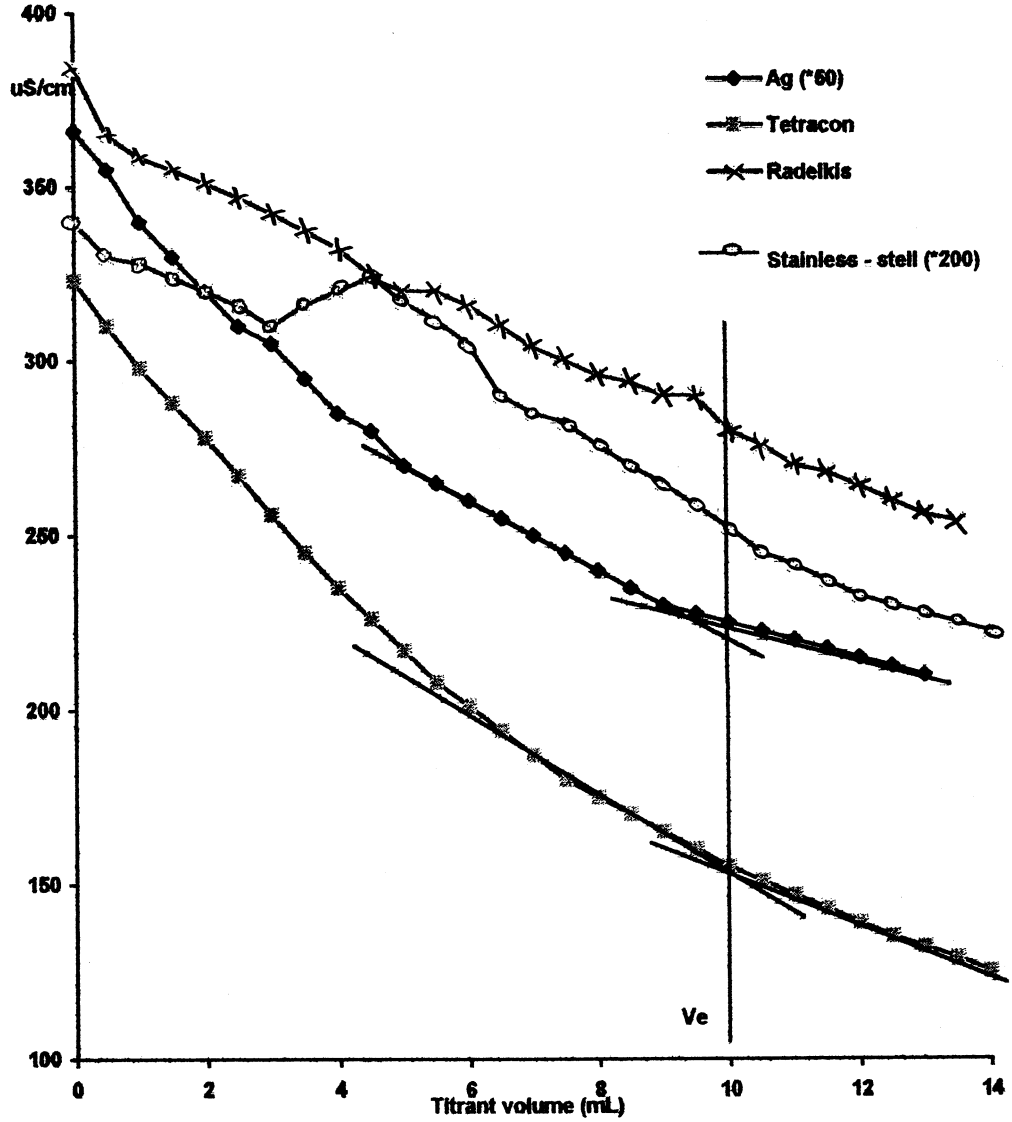


Fig. 1. Curves of conductometric titration of Pb^{2+} with MATD using cells with different electrodes.

3. Results and discussion

3.1. Conductometric study of the reactions between Pb^{2+}, Cd^{2+} and 2-mercapto-5-R-amino-1,3,4-thiadiazole derivatives

The equivalence point, respectively the equivalence volume obtained with silver spiral electrode are comparable with the values obtained with graphite electrodes (Tetracon 96) within the accepted experimental errors. In the case in which stainless steel spiral electrodes were used, it is more difficult to seize the equivalence point, because of the polarisation of the electrode. This fact made us give up using this conductivity cell. The Pt-platinated Radelkis electrode does not enable us to highlight accurately the equivalence point, either. The imprecision of the determinations is probably due to the adsorption of the

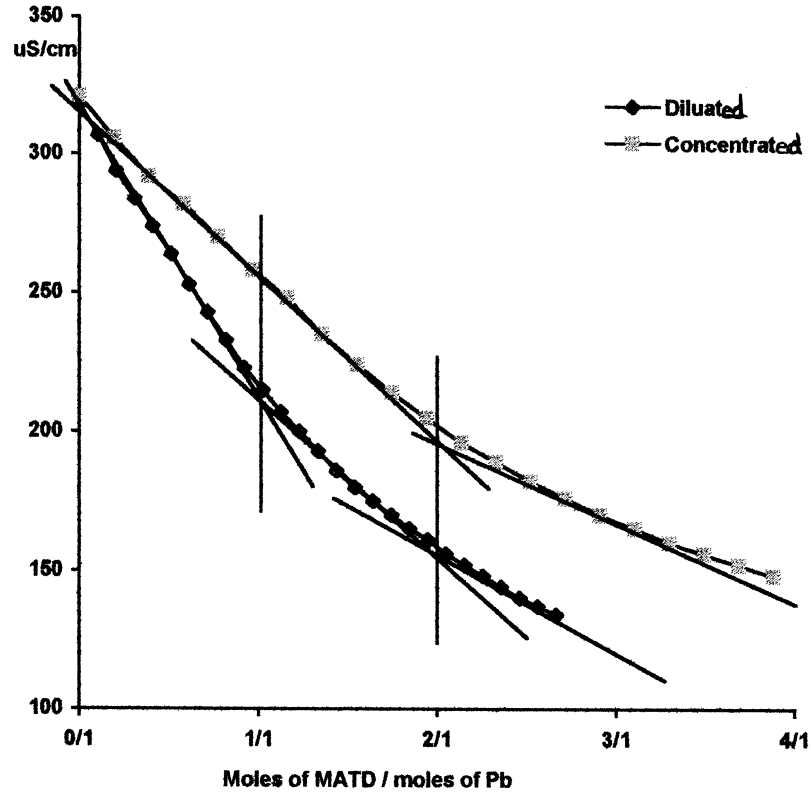


Fig. 2. Curves of conductometric titration of $Pb(NO_3)_2$ with MATD in different pH conditions.

precipitate on the surface of the adherent lever of Pt black; this fact gives more serious errors of determination.

The most sensitive electrode proved to be Tetracon 96. In this case, the conductibility variations highlighted at the equivalence are clear and the experimental errors are smaller; that is why we use for the quantitative determination the Microprocessor Conductivity Meter LF 537 with Tetracon 96 electrode (Fig. 1).

The titrations were performed in an unbuffered environment and as a comparison, in the presence of 0.1 M CH_3COONa, to ensure the optimal pH in order to achieve the quantitative precipitation of the cation with the reagents studied. (Fig. 2) As the products resulting from the reaction are insoluble ($P_s = 10^{-14}$), the concentration of reagents in the thiolic form is enough to enable the quantitative precipitation of the metal ions [4]. It is noticed that in case of titration at pH $\approx$ 6.5 the conductibility variations are more obvious and the equivalence point can be more accurately highlighted. For this reason, for the quantitative determination of the two ions by conductometric titration were used buffer solutions.

Titration curves by graphically representing the conductivity values according to the volume of the titrant solutions are shown in Figs. 3 and 4. The equivalence values were calculated by intersecting the most probable curves.

In all the cases, the conductibility values decreases both before and after reaching the equivalence point. It is noted that in concentrations higher than 10^{-2} M, the titration curves obtained in all cases (regardless of the conductivity cell used) have only one inflexion point which is well highlighted, well defined, corresponding to the 1:2 molar ratio of Me^{2+}:R, corresponding to the one calculated. To concentrations lower than 10^{-2} M, the titrations curves present two distinctive inflex-

ion points, corresponding to the molar ratio Me:R = 1:1 and 1:2, respectively. This shows the step formation of two compounds, according to the general reaction previously mentioned (Fig. 3).

The initial conductibility is high, because $Pb(NO_3)_2$ is dissociated. As we add the titrating solution (an organic compound with a low acid character, slightly dissociated) the mobility decreases (the strong acid which is formed is tamponated by CH_3COONa).

The shape of the titration curves indicates conductivity values decrease more and more. The decrease of the conductivity is more clear in the first part of the curve, until the compound having the molar ratio 1:1 is formed. The second molecule of the reagents modifies the curve inclination a little up to an inflexion point corresponding to the formation of the stoechiometric compound 1:2. After this, the curve shows a constant value of the conductivity. The slightly decreasing curve which is noticed after the inflexion point corresponding to the second equivalence point, can be explained by the effect of adding the reagent in excess.

The conductometric study of the reactions between Pb^{2+}, Cd^{2+} and 2-mercapto-5-*R*-amino-1,3,4-thiadiazole derivatives gives new evidence for elucidating the structure and the composition of the metallic compounds with the reagents studied. The results correspond to those obtained by the potentiometric and spectral methods and by elementary chemical analysis. These determinations confirm the formation of metallic compounds in a 1:2 ratio of Me^{2+}:R.

3.2. The quantitative determination of Pb^{2+} and Cd^{2+} with 2-mercapto-5-R-amino-1,3,4-thiadiazol by conductometric method

The quantitative analysis by conductometric method is based up on the linear relation between the concentration of the metallic ion in solution and his contribution to the total conductivity of the

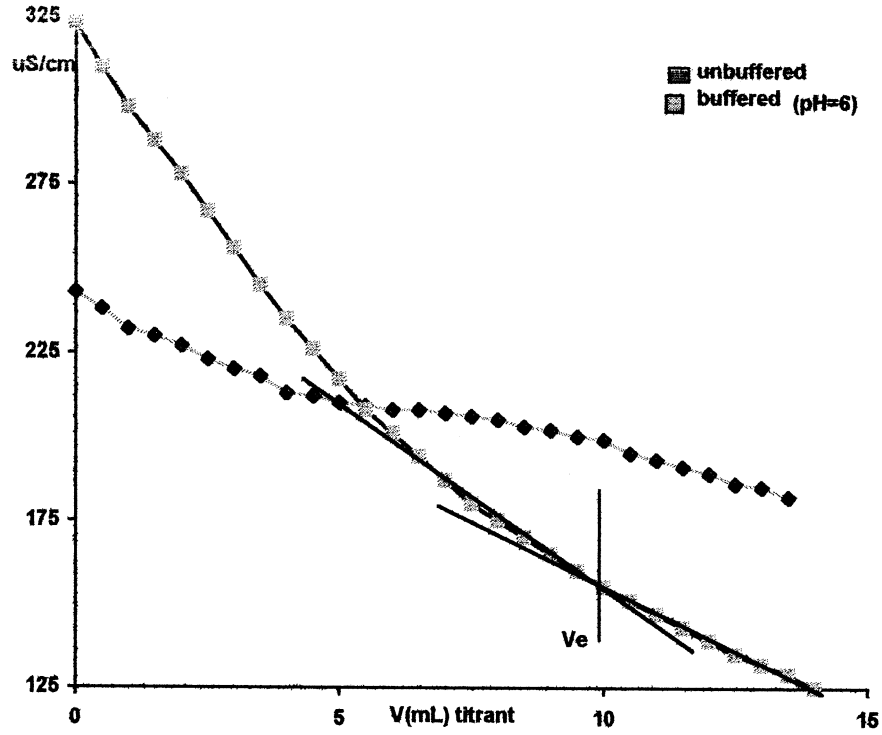


Fig. 3. Comparative representation of the curves of conductometric titration into diluted (10^{-4}–10^{-2} M) and concentrated ($>2\times10^{-2}$ M) solutions.

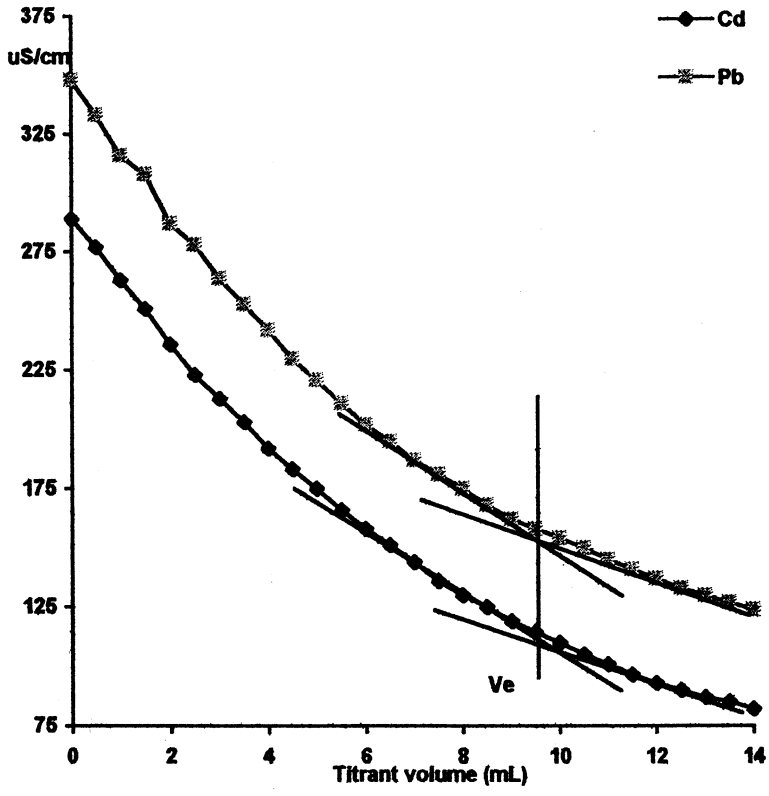


Fig. 4. Curves of conductometric titration of 5 ml $Pb(NO_3)_2$ 10^{-2} M and 5 ml $Cd(CH_3COO)_2$ 10^{-2} M with MFATD 10^{-2} M.

Table 1
The linearity data of the conductometric titration

Reagents	Pb^{2+}	Cd^{2+}
MATD	$y_1 = (267 \pm 2.88) - (11.33 \pm 0.35)x$ $r = 0.9962$	$y_1 = (233 \pm 2.95) - (10.60 \pm 0.37)x$ $r = 0.9936$
	$y_2 = (229.15 \pm 1.64) - (7.46 \pm 0.13)x$ $r = 0.9989$	$y_2 = (190.75 \pm 1.22) - (6.28 \pm 0.10)x$ $r = 0.9997$
MAlATD	$y_1 = (225.23 \pm 2.87) - (5.6 \pm 0.17)x$ $r = 0.9966$	$y_1 = (169.97 \pm 1.67) - (4.34 \pm 0.11)x$ $r = 0.9988$
	$y_2 = (107 \pm 1.55) - (2.82 \pm 0.06)x$ $r = 1$	$y_2 = (149 \pm 1.60) - (3.28 \pm 0.06)x$ $r = 0.9991$
MAcATD	$y_1 = (257.57 \pm 2.74) - (10.43 \pm 0.33)x$ $r = 0.9964$	$y_1 = (216.27 \pm 0.59) - (11.45 \pm 0.7)x$ $r = 0.9974$
	$y_2 = (201.91 \pm 1.42) - (5.64 \pm 0.12)x$ $r = 0.9975$	$y_2 = (171.83 \pm 1.38) - (6.90 \pm 0.3)x$ $r = 0.9982$
MFATD	$y_1 = (274.26 \pm 3.56) - (12.28 \pm 0.43)x$ $r = 0.9958$	$y_1 = (232.85 \pm 2.4) - (12.64 \pm 0.3)x$ $r = 0.9986$
	$y_2 = (211.33 \pm 2.14) - (6.67 \pm 0.25)x$ $r = 0.9969$	$y_2 = (165.82 \pm 3.22) - (6.52 \pm 0.28)x$ $r = 0.9949$

$y = b - ax$, including the SD of the slope and the interscept.
x is the titrating volume (ml) and y is the conductibility (μs cm^{-1}).
Five replicate samples for conductometric titration of 5 ml Me^{2+} 10^{-2} M

Table 2
Conductometric titration data of Cd^{2+} at 1:2 ratio of Cd^{2+}:R

Reagents	Cd^{2+} weighed (mg ml^{-1})	Cd^{2+} found[a] (mg ml^{-1})	Recovery (%)	RSD (%)	Statistical parameters
MATD	0.0111	0.0110	99.29	0.22	Confidence limits: 99.58 ± 0.15 ($n = 15$; $t = 2.145$; $\alpha = 0.95$); linearity: $y =$
	0.1114	0.1111	99.82	0.17	$49.833x + 29.6206$, $r = 0.9948$; fidelity: test Cochran: C (calculated): 0.53, C (0;
	0.5569	0.5542	99.51	0.28	0.5; 3;. 5): 0.707; repeatability $CV_r = 1.145$; reproducibility $CV_R = 1.195$
	1.1139	1.1117	99.80	0.08	
	2.2278	2.2167	99.50	0.20	
MAlATD	0.0111	0.0110	99.27	0.21	Confidence limits: 99.68 ± 0.22 ($n = 15$; $t = 2.145$; $\alpha = 0.95$); linearity: $y =$
	0.1114	0.1114	100.02	0.16	$39.505x + 28.92$, $r = 0.9861$; fidelity: test Cochran: C (calculated): 0.596, C (0; 0.5;
	0.5569	0.5555	99.76	0.72	3;. 5): 0.707; repeatability $CV_r = 1.768$; reproducibility $CV_R = 2.2$;
	1.1139	1.1116	99.80	0.08	
	2.2278	2.2183	99.58	0.24	
MAcATD	0.0111	0.0109	98.88	0.20	Confidence limits: 99.08 ± 0.31 ($n = 15$; $t = 2.145$; $\alpha = 0.95$); linearity: $y =$
	0.1114	0.1096	98.39	0.36	$54.328x + 33.342$, $r = 0.9938$; fidelity: test Cochran: C (calculated): 0.702, C (0;
	0.5569	0.5517	99.07	0.43	0.5; 3;. 5): 0.707; repeatability $CV_r = 1.93$; reproducibility $CV_R = 2.14$
	1.1139	1.1104	99.69	0.03	
	2.2278	2.2123	99.30	0.04	
MFATD	0.0111	0.0111	100.07	0.15	Confidence limits: 99.87 ± 0.11 ($n = 15$; $t = 2.145$; $\alpha = 0.95$); Lineariy: $y =$
	0.1114	0.1112	99.85	0.29	$49.436x + 21.272$, $r = 0.9902$; fidelity: test Cochran: C (calculated): 0.405, C (0;
	0.5569	0.5555	99.75	0.14	0.5; 3;. 5): 0.707; repeatability $CV_r = 0.997$; reproducibility $CV_R = 2.720$
	1.1139	1.1117	99.80	0.16	
	2.2278	2.2248	99.86	0.21	

$y = ax + b$ Where x is the concentration (mg ml^{-1}) and y is the conductibility (μs cm^{-1}) at the equivalance point.
[a] Average of three determinations.

Table 3
Conductometric titration data of Pb^{2+} at 1:2 ratio of Pb^{2+}:R

Reagents	Pb^{2+} weighed (mg ml^{-1})	Pb^{2+} found[a] (mg ml^{-1})	Recovery (%)	RSD (%)	Statiscal parameters
MATD	0.0211	0.0210	99.63	0.32	Confidence limits: 99.60 ± 0.16 ($n = 15$; $t = 2.145$; $\alpha = 0.95$); linearity: $y = 38.106x + 76.147$, $r = 0.9926$; fidelity: test Cochran: C (calculated): 0.44, C (0; 0.5; 3;. 5): 0.707; repeatability $CV_r = 0.598$; reproducibility $CV_R = 2.53$
	0.2114	0.2107	99.70	0.20	
	1.0572	1.0584	99.39	0.46	
	2.1143	2.1058	99.60	0.18	
	4.2289	4.2145	99.66	0.28	
MalATD	0.0211	0.0211	100.03	0.02	Confidence limits: 99.66 ± 0.16 ($n = 15$; $t = 2.145$; $\alpha = 0.95$); linearity: $y = 39.571x + 77.56$, $r = 0.988$; fidelity: test Cochran: C (calculated): 0.756, C (0; 0.5; 3;. 5): 0.707; repeatability $CV_r = 0.713$, reproducibility $CV_R = 4.73$
	0.2114	0.2108	99.75	0.15	
	1.0572	1.0516	99.47	0.42	
	2.1143	2.1054	99.58	0.25	
	4.2289	4.2082	99.51	0.14	
MacATD	0.0211	0.0211	100.01	1.14	Confidence limits: 99.83 ± 0.16 ($n = 15$; $t = 2.145$; $\alpha = 0.95$); linearity: $y = 35.158x + 74.197$, $r = 0.9945$; fidelity: test Cochran: C (calculated): 0.405, C (0; 0.5; 3;. 5): 0.707; repeatability $CV_r = 0.997$; reproducibility $CV_R = 2.270$
	0.2114	0.2110	99.83	0.31	
	1.0572	1.0544	99.71	0.51	
	2.1143	2.1102	99.81	0.35	
	4.2289	4.2175	99.77	0.21	
MFATD	0.0211	0.0211	100.11	0.11	Confidence limits: 99.86 ± 0.13 ($n = 15$; $t = 2.145$; $\alpha = 0.95$); linearity: $y = 37.00x + 78.70$, $r = 0.9906$; fidelity: test Cochran: C (calculated): 0.64, C (0; 0.5; 3;. 5): 0.707; repeatability $CV_r = 0.66$; reproducibility $CV_R = 2.214$
	0.2114	0.2106	99.57	0.13	
	1.0572	1.0548	99.78	0.15	
	2.1143	2.1158	100.02	0.14	
	4.2289	4.2211	99.82	0.18	

$y = ax + b$ Where x is the concentration (mg ml^{-1}) and y is the conductibility (μs cm^{-1}) at the equivalance point.
[a] Average of three determinations.

solution [6–10]. Accurate conductometric determinations can be made using the second break points of the titration curves as equivalence points, in the range of Me^{2+} concentration 10^{-2}–10^{-4} M. Thus, the conductometric titrations of Pb^{2+} and Cd^{2+} were performed on five concentration levels of Me^{2+} solutions. In each series at least three titrations were carried out with each of the ligands used as analytical reagents, in the above mentioned conditions.

The shapes of the titration curves of the two cations are similar. The curves are also similar whichever of the four reagents studied is used as titrant. In the analytical study of the results we took into consideration the intersection of the lines corresponding to the ratio molar 1:2 (Me^{2+}:R). The equivalence volume was established at the intersection of the most probable lines (the linearity coefficient is 0.99) (Fig. 3). The extended data of the linearity for the shape which determine the equivalence point are present in Table 1.

In Tables 2 and 3 we presented the results obtained in the quantitative determination of the two metal ions by conductometric titration with four derivatives of 2-mercapto-5-*R*-amino-1,3,4-thiadiazole as well as the statistical parameters obtained after processing according to the validation methodology (Tables 2 and 3).

The specificity and the accuracy of the procedure do not depend on the nature of the anions. The preliminary studies performed on different metal salts (nitrate, acetate, chloride) have revealed that no significant differences are observed (the shape of the titrations curves is the same and the analytical results are similar). But the quantitative determination based on these reactions are influenced by the anions which form insoluble combinations with the cations studied (S^{2-}, SO_4^{2-}). The other metal ions (Ag^{+}, Hg^{2+}, Cu^{2+}, Bi^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}) interfere with the proposed procedure, but only in concentrations higher than 10^{-4} μg ml^{-1}. Also, the quantitative determination of Pb^{2+} in the presence of Cd^{2+} is possible only applying the masking (and demasking) techniques.

The quantitative determination of Pb^{2+} and Cd^{2+} can be used for the determination of these cations in biological and/or environment samples with application to the determination of polluting and toxic cations (after a previous pre-treatment and preconcentration of the sample).

4. Conclusions

The conductometric study carried out on the reactions between Pb^{2+}, Cd^{2+} and 2-mercapto-5-*R*-amino-1,3,4-thiadiazole confirm the results obtained by elementary chemical analysis, along with the formation of the metal compounds in the stoechiometric ratio 1:2 of Me^{2+}:R.

In order to compare the results, in the same conditions, the conductometrical titrations were performed with four different conductivity cells, the most sensitive electrode being Tetracon 96.

The quantitative analysis of Pb^{2+} and Cd^{2+} is based on the reaction of conductometric titrations and it can be applied in the range of Me^{2+} concentration 10^{-1}–10^{-4} M. For concentrations lower than 10^{-2} M titration curves with two distinctive inflection points were noticed, corresponding to the molar ratio Me^{2+}:R = 1:1 and 1:2, respectively. Thus, two compounds were formed gradually, the latter being used in quantitative determination.

The method proposed enables the quantitative determination of Me^{2+} within the error limits accepted by the validation standards (lower than 1%). The coefficient of repeatability (CV_r) and reproducibility (CV_R) were calculated for the samples ($n = 15$); the fidelity parameters is according with the validation norms.

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