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The Determination of Some Heavy Metal Cations by TLC/Photodensitometry

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The samples having complex matrices were analyzed for some heavy metal cations by using a thin layer chromatography/photodensitometry (TLC/PD) system. The rock samples were dissolved by suitable methods. Nickel, Cobalt and Copper were dedected and analyzed by photodensitometric comparison of corresponding spots of samples with those of standards. The results of the same samples and standards were compared with those obtained by atomic absorption measurements. Our results are comparable with the results of flame atomic absorption measurements. The precision of TLC method was calculated to be 9.4% as relative standard deviations depending on 17 replicate measurements. The accuracy of TLC method was also controlled by analyzing a standard reference material (SRM) NIES No 2). The method exhibits about-2%-38% relative errors.

Introduction

It is well known that chromatographic techniques are unique for separation and purification purposes. Besides with the aid of modern efficient dedectors, chromatography has also become a powerful tool of identification and determination. Inorganic chromatographic applications however are still very limited comparing with those of organic and biochemical applications. Only 5% of all chromatographic literature related to inorganic species and applications are limited to their simple aqueous solutions [1].

In this work it was aimed to study the applicability of TLC to the samples having complex matrices. Thus, it was expected to gain the following chromatographic advantages to overcome the lack of AAS, AES and, to produce an alternative to photometric methods in inorganic analysis. First, TLC is a convenient and inexpensive method of analysis. Secondly it provides the possibilities of determinations of many analytes or analyses of multisamples simultaneously on a single chromatographic plate. Furthermore, it can be identified and determined the different oxidation states of the cations by TLC, while it only could be measured total concentrations by AAS or AES.

AAS is a sequential analysis technique which requires a specific lamp for each definite element and it can only determine total concentration of the element. During the trace analysis by AAS sometimes it may be necessary for an equal enrichment processes to all of chromatographic procedures. On the other hand, because of excess reactant's consumption photometric methods are expensive, labor intensive, and time consuming methods.

Diethyldithiocarbamates were chosen as chelating reactants for reasons of convenient chromatographic separation, simultaneous determination and successful group extraction.

Experimental

Samples

Two rock samples were characterized and analyzed as rock 1 and rock 2. The samples were dissolved and prepared by standard procedures of AAS analysis [2,3,4]

Chelating Reagent and Formation of Chelates

The properties of chelating reagent are important for analytical and particularly for chromatographic purposes [5].

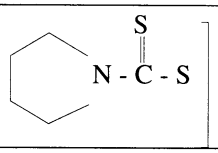
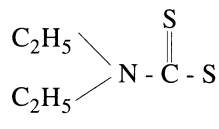
An important step is the choice of a chelating reactant for the liquid adsorption chromatography (LAC) in which metal complexes are applied on water vapour saturated TLC plates. The criteria of choosing a chelating reactant are as fallow:

1. The chelating reactant must react with most of the metal cations to give strong complexes,
2. the complexes must be coordinatively saturated,
3. the donor atoms should have lower total electronegativity,
4. the substituent groups must have lower inductive and steric effects,
5. the electronegative atoms must be in the neighborhood of chelate ring,
6. the complexes must have high thermodynamic stability,
7. in contrast to the ligand, the complexes must significantly be dissolved in apolar solvents and
8. the complexes must have intensive UV or visible absorption bands

The diethyldithiocarbamates could be the most suitable chelating reactants, in view of above expected properties [6,7].

Here, sodiumdiethyldihtiocabamate (NaDEDTC) and ammoniumpyrrolidinedithio carbamate (NH_4P_y DTC) were used as chelating reagent (Table 1). Dithiocarbamates easily reacts with most of the transition metals giving stable chelates. These are neutral and relatively apolar complexes [6,7].

Table 1. The Chelating Reagents

Reagent	Formulas	Abbreviations
Ammoniumpyrrollidinedithiocarbamate		NH_4PyDTC
Sodiumdiethyldithiocarbamate		NaDEDTC

Stock ligand solutions of 10 g L^{-1} were prepared. Standard cation solutions were also prepared from the corresponding nitrate and chloride salts (Merck). The chelating procedure was carried out in two ways:

1. Prechromatographic chelate formation on the plate.
2. Chelate formations in aqueous media.

1. Prechromatographic Chelate Formation On The Plate: It was performed either by injections of analyte and ligand solutions at the same origin on the plate or by application of analyte on the plate and adding ligand solution to the solvent. The former procedure has the disadvantage of two successive applications might cause punching of the chromatographic plate's coating. The second procedure prevents this disadvantage. Furthermore, it is simple and rapid. However, the procedure may not be appropriate for every analyte's concentrations since it is not possible to preconcentrate the analyte in this procedure.

2. Initially Chelate Formation In An Aqueous Medium: The analyte and standard solutions were treated with the ligand solutions at pH=5.5-6, adjusted by acetic acid/sodium acetate buffer. The the complexes extracted to chloroform phase at $pH < 7$[8]. Thus the advantages of preconcentration and cation selection were gained at the sametime. Furthermore in this way the chromatographic tailing and hence scattering of R_f values with the removal of complex associated in organic phase were prevented. The chloroform was used as organic phase for reasons of providing an additional stability to the chelates [9].

The organic phase was dried by treating with anhydrous-Na_2SO_4.

Chromatographic Procedures

In this study we used home-coated and commercial silica plates. The plate coating materials (silica 60G, -60H, -60GF$_{254}$, -60HF$_{254}$ -60PH$_{254}$) and the commerical plates were suppplied from Merck Company. The injection of samples and standards on the plates were carried out by using disposable tip Fisher pipettes. The solvents of dichloromethane petroleum ether, benzene, and toluene either separately or in mixtures forms are used as plate developer. The dichloromethane: petroleum ether (9: 1) was selected as an optimum mobile phase for running of the complexes. Therefore this mixture was used in the subsequent parts of this study.

The possibility of specifying Cu(II)/Cu(II)Cu(I); Fe(III)/Fe(II); Hg(II)/ Hg(I); Sb(V)/Sb(III) and Mn(IV)/Mn(II) cation pairs were determined.

The Densitometric Quantitative Analysis

The chromatographic quantitation procedures of classical techniques are non-sensitive, labor intensive and tedious. Furthermore they have poor precisions. For example, the error is about 30% in quantitative evaluation by eye depending upon the comparison of color intensities of standard and sample spots on the chromatographic plates. The measurement technique of the 'spots' area as a measure of concentration by using a planimeter has also an error of about 10%.

The photodensitometric method becomes an important tool for quantitation of TLC spots. The TLC plates can be scanned linearly, zigzag, circularly and diagonally in particularly for irregular chromatograms at reflection, florescence and transmission modes. The scanning can be performed with 2% relative standard deviations by using modern HP TLC instruments [10].

In this study the Cu(DEDTC)$_2$, Ni(DEDTC)$_2$ and Co(DEDTC)$_2$ spots on commercial TLC plates were determined by using a Shimadzu CS 9000 model densitometer[11]. The spots were measured in the zigzag scanning and reflection mode, and by background correction function. The spot areas are converted into concentration and the results are automaticaly printed.

The Selection of Densitometric Reflection Wavelength: For quantitative analysis of the spots a wavelength selection is necessary at which the chelat interested in must exhibit a maximum reflection. The wavelength selection was carried out by scanning of certain spots with different wavelengths. Thus wavelengths showing maximum reflections, for Cu-, Ni-and $Co(DEDTC)_2$ are given in Table 2.

Table 2. The wavelengths used for the measurement of densitometric reflections of chelat spots

The Chelates	working wavelengths/nm
$Cu(DEDTC)_2$	273
$Ni(DEDTC)_2$	328
$Co(DEDTC)_2$	325

The Samples and Standards: The rock, mine, and sediment samples were prepared for FAAS and TLC/Photodensitometer by the following procedures. The standard solutions of the concerning cations were prepared from nitrate and chloride salts and the solution matrices were matched by adding appropriate amounts of needed chemicals.

Fusion With Na_2O_2: The aliquots 2.000 g of rock 1 and 2 samples were dissolved by fusion with sodium peroxide and the diluted to 250.0 mL. The 0.5000 g samples of chromite (chromite 1, chromite 2 and chromite 3) fused with sodium peroxide in the nickel crucibles and the residue redissolved in a volume of 25.0 mL of 1% HCI and then diluted to 500.0 mL.

Dissolving the Samples in the Mixture of HNO_3, HF and $HCIO_4$: The 0.2000 g samples of rock 1 and rock 2 were dissolved in a mixture of HNO_3, HF and $HCIO_4$ in , (v/v) 5:2:2; ratio evaporated and the solid residue redissolved in 1% HCI and then diluted to 200.0 mL.

Disolving in Aqua Regia: The 0.1000 g samples of mine dissolved in aqua regia filtrated and the supernatant liquid diluted to 100.0 mL.

Dissolving in H_2SO_4: The 5.000 g samples of chromite was reacted with 250.0 mL $H_2SO_4(200gL^{-1})$ for 240 minutes and a volume of 0.5 mL of the supernatant diluted to 100.0 mL.

Dissolving in an Acid Bomb: The pool sediment reference standard material (NIES 2) dissolved in the mixture of HNO_3, HF and $HCIO_4$, in (v/v) 12:4:4 ratio in an acid bomb as recommended by NIES (National Institute of Environmental Studies) and the supernatant diluted to 50.0 mL.

Results and Discussion

Silica 60 G and a mixture of dichloromethane and petroleum ether were found to be most suitable adsorbent and solvent system, respectively.

The separations of Cu(II), Ni(II), Co(II), Sb(II), Sb(V), Hg(II), Hg(I) and Cu(I) were satisfactorily accomplished in the sample solutions by using the selcted adsorbent and the solvent system. The other cations could not be separated; the spots were either staying at the application points of the plates or moving with ligand spot.

The cations were identified on plate either by comparing the spots with the known cations spots or by their IR spectra. The precision was computed in term of RSD % and found to be 2.3% for nine replicate measurements, it was found that the precision neither depends on type of cations, nor kind of ligands.

The similar separations could also be performed by active surface TLC with lower R_f values and with slower runs. The spots obtained by active surface TLC were not suitable for quantitation by densitometry.

The separation of the cation pairs of Cu(II)/Cu(I); Hg(II)/Hg(I); and Sb(V) /Sb(III) was satisfactorily

carried out while the separation of the pairs of Fe(III)/Fe(II) and Mn(IV)/Mn(II) were not possible in context of cation specifying.

The pair of $Cu(PyDTC)_2$ and CuPyDTC exhibit the Rf values of 0.59 and 0.45 in toluene: respectively dichloromethane solvent mixture (1:1, v/v). The- PyDTC chelates for the pairs of Hg(II)/Hg(I) and Sb(V)/Sb(III) were separated with the Rf values of 0.83; 079; and 0.73; 0.89, respectively, by using a dichloromethane petroleum ether as solvent sytem.

The applications of LAC given in the literature are mainly on samples of having simple matrices such as standards, water and waste water [12,13]. These type of applications are used for chromatographing the dithiocarbamate of cations in aqueous phase. However, we could not fund applications of TLC to complex matrices of geological, mine, rock and aqueous sediments which particularly can be expected to be efficient in the analyses of these samples. As a simple example of analyzing the complex matrix samples by TLC there cations namely Cu(II), Ni(II) and Co(II) were chosen, so that they can be significantly separated from each other and hence cause no trouble during quantitation on plates.

The sample matrix and the TLC/PC concentrations are given in Table 3 and compared with FAAS concentration.

Table 3. The Matrix Properties of the Samples and the Analyses Results for Cu,Ni and Co by TLC/PD Compared with Those of FAAS

		Results of Analyses					
		*FAAS,ppm			TLC/PD, ppm		
Samples	Samples Matrices	Cu	Ni	Co	Cu	Ni	Co
Rock 1	15% Al,Ca,Mg,Na,Fe	0.10±0.01	0.10±0.01	0.10±0.01	0.20±0.02	-	-
Rock 2	19% Al,Ca,Mg,Na,F	0.05±0.00	0.10±0.01	0.10±0.01	-	-	-
Rock 3	11% Al,Ca,Mg,Na,Fe	15.0±0.9	0.10±0.01	0.10±0.01	12±1	-	-
Chromite 1	45% Cr_2O_3; 12% FeO; 8% Al_2O_3 and 12% MgO	0.20±0.01	51.0±2.9	0.70±0.04	0.23±0.02	60±6	0.51±0.05
Chromite 2	24%Cr_2O_3; 10%FeO;7%Al_2O_3 and 23%MgO	1.10±0.06	38±2	0.80±0.05	1.50±0.14	47±4	0.67±0.06
Chromite 3	38%Cr_2O_3, 12%FeO;7%Al_2O_3 and 23%MgO	-	28±2	0.60±0.03	-	33±3	0.47±0.04
Mine	13%MnO; 14%Al_2O_3,6%Fe_2O_3; 0, 7% TiO;14%CaO	11.0±0.6	-	-	12.5±1.2	-	-
Pool sediment	11% Al;7%Fe;1%Ca,1%Na	200±11	32±2	18.0±1.0	118±11	21.0±2.0	15±2
(NIES** No2)		210±12	40±2	27±3			

* Obtained by CU Eng. Fac. Geological Laboratory.

** National Institute of Environmental Study[14]

The accuracy and the precision of our method controlled by determining the content of Ni, Cu and Co in complex matrix samples by following procedures.

Controlling the Accuracy of the Method: The accuracy was controlled by analyzing a standard reference material (SRM) and the results were compared with those of FAAS for the same samples under the same conditions.

The method exhibited negateive determination errors for the SRM samples of three cations, namely -35.2% for Co,-43.8% for Cu and -47.8 % for Ni. We concluded that the serious error arises from the prechromatographic steps of the analysis. That is, the analytes might be lost, mainly at dissolving step and partially at the extraction step. An evidence of this deduction, can be seen considering the results of FAAS analysis which also exhibited negative errors for the mentioned cations, namely -33.0% for -5.0% for Cu and -20.0% for Ni. Correcting the results of FAAs, the errors -38.8% for Cu; -27.5% for Ni and -2.2% for Co may be obtained. We can say that the errors observed for Cu and Ni are significant while the error for Co is in an acceptable level. Furthermore, the difficulty of dissolving the sediment samples is reported by NIES[14]. Then the errors in determining Cu and Ni can be attributed to the complextion and extraction steps rather than chromatographic procedures.

The comparison of the results of our method with those of FAAS for the samples prepared in the

same way was another criterion of the accuracy of the method. The half of the results of TLC/PD were higher than those of FAAS, while the other half of them were lower. So it can be concluded that there are no significant differences between the two groups of results. The situation is seemed obviously a reproducibility problem.

Controlling the Precision of the Method: It is found that a collected standard deviation of 9.4 was calculated as percent in term of relative standard deviation as a measurement of the reproducibility, applying to a total of 17 measurements of 7 samples [15]. The relatively poor reproducibility of this method was mainly attributed to the manual sample injections step. We believe this problem can be overcome by automatic injection.

Conclusion

TLC/PD technique may be a convenient, speedy, inexpensive alternative method for the photometric method [16]; and also covenient and available alternative to AAS for small budged laboratories. TLC/PD also offers the possibilities of simultaneous multielement determinations on very small amounts of samples compared with FAAS[17,18]. OF course, the performance of the proposed method will be improved with additional investigations.

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