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REAGENTS WITH CHELATANT ACTION FOR Pb (II) AND THE POSSIBILLITY OF USING THEM IN FLOTATION

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ABSTRACT. In this paper we followed up the data corelation of analitical chemistry of complexation for Pb (II) with chelatants in aqueous solution and the collector power of these reagents in the flotation of the minerals cerusite and galena that contain this ion.

INTRODUCTION

Reagents with chelatant action are used in analytical chemistry due to their selectivity to certain metal ions in solution [1]. In the formation and stability of the chelated cycles the following factors have an important role: the pH of the solution, the basicity of the ligants, the size and number of the chelated cycles, the resonance effect and the steric effects.

The following reagents with chelatant action that form chelat compounds with the ion Pb (II) in solution have been studied: 8-hydroxyquinoline (oxyne), eriochrome black T, acetylacetone, 2 hydroxyphenyl azonaphtol 2 ,2 hydroxytrimethylene-diaminotetraacetic acid.

The stability of the complex obtained between the cations and the ligants depends on the pH, the modifications resulting from the variation of the pH being characterised by the apparent constant of formation, K'.

We have taken into consideration the curves of variation log K' depending on the pH for the chelatant systems Pb (II) and Ca (II).

The role of the chelatic compound in the separation of minerals by flotation is increasing [2 - 5]. In the choice of flotation reagents it is considered that their fixation on the surface of the minerals takes place, in many cases, through chemical links between the superficial center of adsorbtion and the reagent, obtaining the chelat compounds. Because of this we can expect the reagent which has proved specific with a metallic ion in solution, to keep its selectivity in certain conditions, in the case of adsorbtion over the surface of the minerals that contain this metallic ion.

We followed the collecting action over both galene (PbS) and on ceruzite ($PbCO_{3)}$ to check how both the mineralogical form and the nature of the anion, influence the action of the collectors. The calcite that usually accompany the minerals in ores, should float very little with these reagents. To check this, the reagents with chelatant action were tested in parallel with calcite.

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To study the collecting action of the reagents with chelatant action we used the flotation which has been done in the Hallimond cell. The experiments were orientated towards the determination of the optimum conditions necessary for a good recovery, the concentration of the reagent and the pH domain.

I.R. spectroscopic detemination have also been used for surveying the formation of certain species at the surface of minerals during adsorbtion of various reagents and there are many reports on this subject [6-12].

The nature of the compounds formed with the action of 8-hydroxyquinoline on ceruzite had been also studied using the I.R. spectroscopy.

EXPERIMENTAL

The Hallimond cell used is an instrument of pneumatic microflotation showed in figure1.

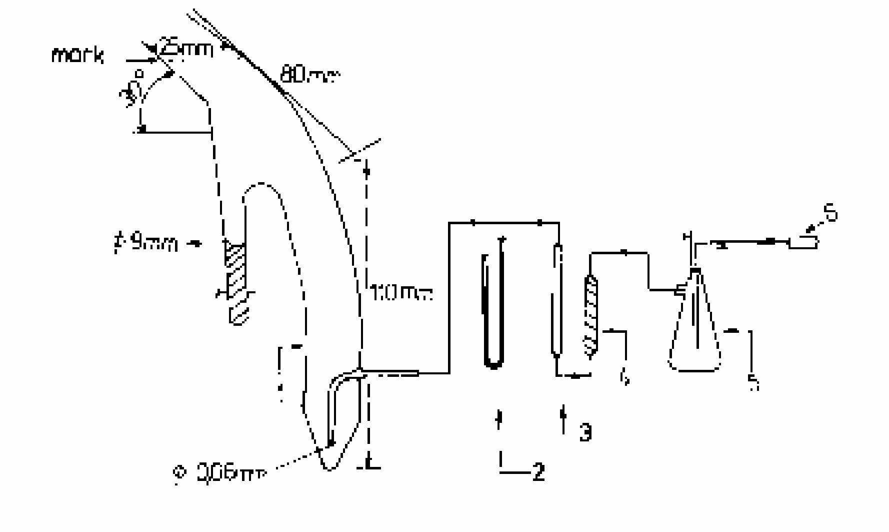


Figure 1. Instalation of microflotation: 1. Hallimond cell; 2. pressure gauge; 3. rotametre; 4 and 5 washing devices; 6. steam roller.

The minerals used, galene, ceruzite and calcite, had the grading ranging between 100-250 μ.

"A" grams of mineral are introduced in the cell. Then the cell is filled up to the mark with the solution of the pH collector, the concentration and the temperature are constant. At a small debit of air the samples are conditioned, then the debit of air increases and the particles covered by the collector are stimulated to the separation surface solution/air. Here the ballons break and the mineral particles are collected into the lateral vertical tube. Throughout this procedure, conditioning time (180 seconds), flotation time (30 seconds) and debit of air 10l/hour that was regulated from a steam roller, following the values on a pressure gauge and on a rotametre were constant. The flotated product is filtrated, dried in the drying stove at 80^{o}C and weighed with the mass "C". The unflotated product is reccovered just the same having the mass "m". It has been observed that the difference between A and C+m is under 5%. That is why in determinations only C has been weighted.

The procent of recuperation, %R (the extraction in weight or the extraction in concentrate) has been obtained by the raport between the mass of the flotant mineral "C" and the mass of the alimented mineral "A".

$$\%R = (C/C+m) \cdot 100 = (C/A) \cdot 100$$

We have used 1 gram mineral. This means that A = 1 gram.

The preparation of the reagent solutions has been done in 1l marked ballone such as

- 0,23 g eriochrome black T are dissolved in water, it is brought to the mark and a solution $5 \cdot 10^{-4}$ M is obtained.
- 14,5 g oxyne are dissolved in acetone and are brought to the mark; a solution 10^{-1} M is obtained which is diluted to obtain the tested solution.
- 1 g acetylacetone is dissolved in water, it is brought to the mark and a solution 10^{-2} M is obtained which is diluted to obtain the tested solutions.
- 0,023 g 2 hydroxyphenyl azonaphtol 2 are dissolved in 6 cm^3 solution 0,25 N NaOH and 10 cm^3 acetone, 300 cm^3 of water is added and it is stirred after which it is brought to the mark with water.
- for a solution 10^{-2} M 2 hydroxytrimethilenediaminotetraacetic acid 3,223 g reagent in 40 cm^3 solution NaOH 10% is dissolved and then it is brought to the mark. The tested solution is 10^{-4} M and it is obtained by dilution.

The I.R. spectra have been realised using the technique of the potasium bromure tablets for ceruzite, Pb (II) oxynate and ceruzite after being treated with solution of oxyne in acetone.

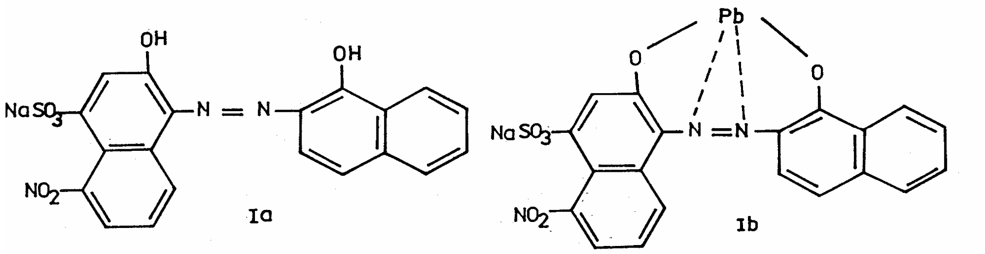
- the natural pure ceruzite has been ground in the agate mortar till 2-10 μ; part of the sample obtained is used to draw the spectrum I.R.; some part of the sample is treated with solution of oxine in acetone for pH = 9, followed by filtration, drying in air and the drawing of the I.R. spectra.
- the Pb (II) oxynate was prepared by using 150 cm^3 aqueous solution of $Pb(CH_3COO)_2 \cdot 3H_2O$ 0,1 M which is treated with 100 cm^3 oxyne 0,3 M solution in acetic acid 10%, it is warmed up and 25 cm^3 oxyne are added; on cooling the pH is established at 10 by NH_4OH, it is filtrated, washed and dried in a drying stove, for one hour at 110^o C.

RESULTS AND DISCUSSIONS

Eriochrome black T

This reagent presents the structure Ia and forms the chelat compound with structure Ib for Pb (II).

The curves from figure 2 indicates the variation of the apparent constant (log K') with the pH for the complexes formed between Pb (II) and Ca (II) with eriochrome black T. A stabillity is noticed, not too big, for Pb(II) in the domain of pH between 7 and 10. Between 6 and 8 allows the separation from the Ca (II).



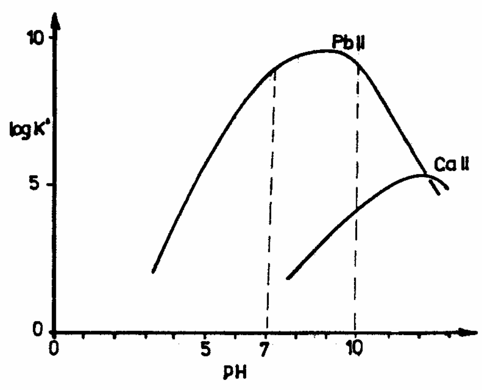


Figure 2. The variation of log K' with the pH for the complexes of eriochrome black T with Pb (II) and Ca (II).

For flotation we used solution 5 $\cdot 10^{-4}$ mol/l in the presence of 0,1 g/l isooctane (for a suitable foam). Figure 3 shows the variation of the recuperation percent, %R depending on the pH for galena, ceruzite and calcite.

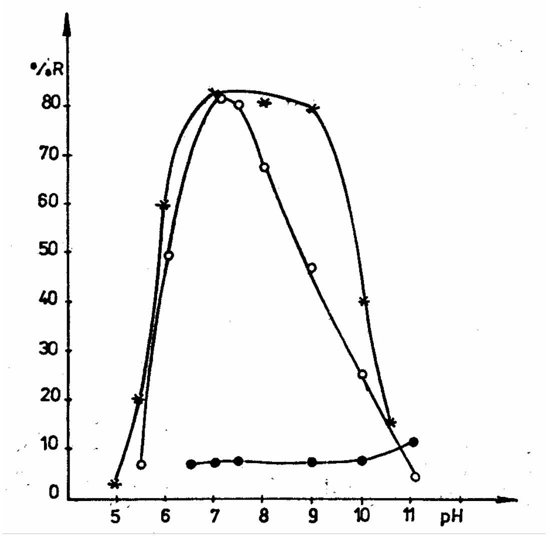


Figure 3. The variation of the recovery procent (%R) depending on the pH for 0,23 g/l eriochrome black T and 0,1 g/l izooctane for:
✱ galene
o ceruzite
● calcite.

It is noticed that eriochrome black T floats with good results for galene and ceruzite, achieving maximum recuperations of 82% for pH = 7. The calcite floats very little. The results are in concordance with the foresights deducted from the data in analitical chemistry.For ceruzite at pH = 7 had determinations been made using reagent solutions of different concentrations in the presence and in the absence of isooctane. The results are presented in Table 1.

Table 1.

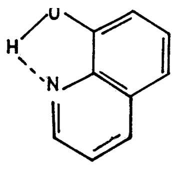
Ceruzite variation %R with the concentration of eriochrome black T solution.

concentration eriochrome black T, mol/l $\cdot 10^{-4}$		0,25	2,5	5	10	15	20
%R ceruzite	with 0,1 g/l izooctane	78	80	82	80	76	74
	without izooctane	12	24	30	28	30	28

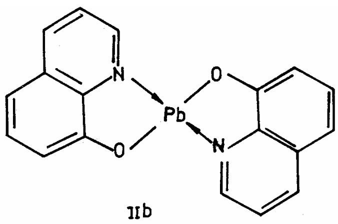
The recuperations are high, 78% even if concentration in the reagent is small, 0,25 $\cdot 10^{-4}$ mol/l in the presence of isooctane.

8 - hydroxyquinoline

This reagent presents the structure IIa and forms with Pb (II) a chelat compound with structure IIb.



IIa



IIb

If the precipitation takes place in solution, the Pb (II) oxynate presents the maximum stability for the pH between 8 and 11, as indicated in figure 4.

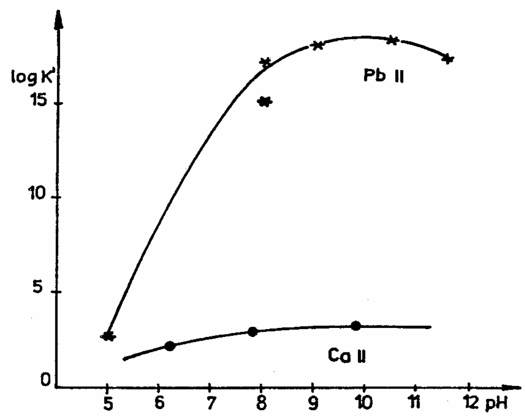


Figure 4. The variation of log K' with the pH for the Pb (II) oxynate and Ca (II) oxynate.

During the determinations in the Halimond cell we have maintained constant the concentration of the oxine, 10^{-3} mol/l, in the presence of 0,1 g/l diesel oil and we have changed the pH from 5 to 12.

Figure 5 shows the variation of the recovery percent depending on the pH for galene, ceruzite and calcite. The maximum recovery of 98% or 100% was obtained for galene with the pH between 8 and 11 and for ceruzite with the pH between 9 and 10. Calcite is to a certain extent floatable with oxyne. Galene and ceruzite float well for the same domaine of pH where the stability of the chelats formed in solution is maximum.

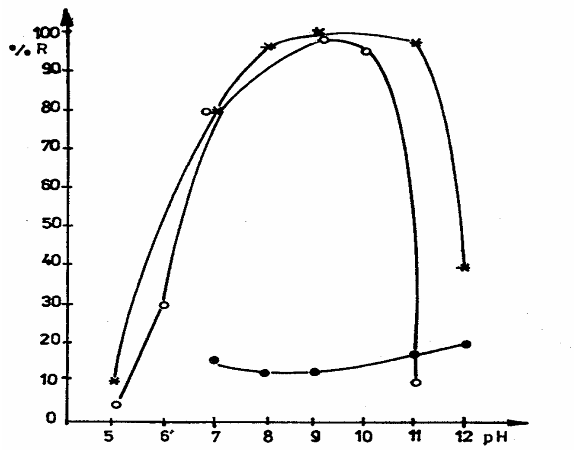


Figure 5. The variation of the recovery percent (%R) depending on the pH with 0,145 g/l oxine and 0,1 g/l diesel oil for:
✱ galene
o ceruzite
● calcite.

For ceruzite with pH = 9 we have followed the variation %R depending on the concentration of the oxyne solution in the presence and in the absence of diesel oil, table 2.The maximum recovery (100%) is obtained only in the presence of diesel oil and at the minimum concentration of 10^{-3} mol/l oxyne.

Table 2.

The variation %R of ceruzite with the concentration of oxyne.

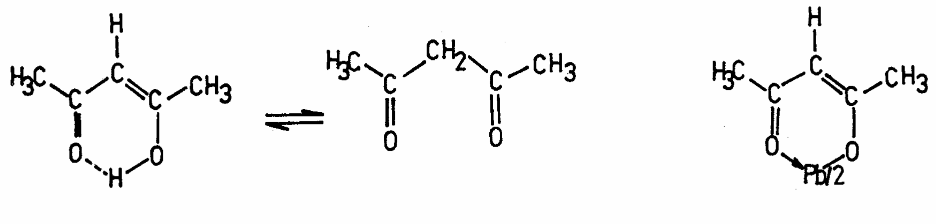
concentration oxyne mol/l $\cdot 10^{-3}$		0,2	0,5	1	2	3	6	8	10
%R ceruzite	with 0,1 g/l diesel oil	10	70	100	98	100	98	30	20
	without diesel oil	2	-	2	-	3	-	-	-

The oxyne has a superior critical concentration of $6 \cdot 10^{-3}$ mol/l because ceruzite is a mineral with a big mass and which, if under concentrations of oxyne forms heavy compounds that reach the surface with great difficulty.

The experiments without diesel oil show that there does not exist a possibbility of ceruzite flotation only with oxyne.

Acetylacetone

It presents the structure IIIa,b and forms the chelate compound with the structure IIIc for Pb (II).



From figure 6 it can be seen that acetylacetonate of Pb (II) has small stability, respectively log K' < 6.

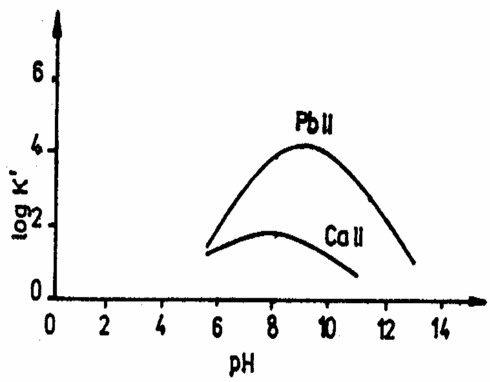


Figure 6. The variation of log K' with the pH for Pb (II) and Ca (II) acetylacetonate.

The tested solution includes 0,5 g/l acetone, that means $5 \cdot 10^{-3}$ mol/l and 0,1 g/l isooctane.We have worked with a pH between 5,5 and 10,5 for galene, ceruzite and calcite. The experimental results are presented in figure 7.

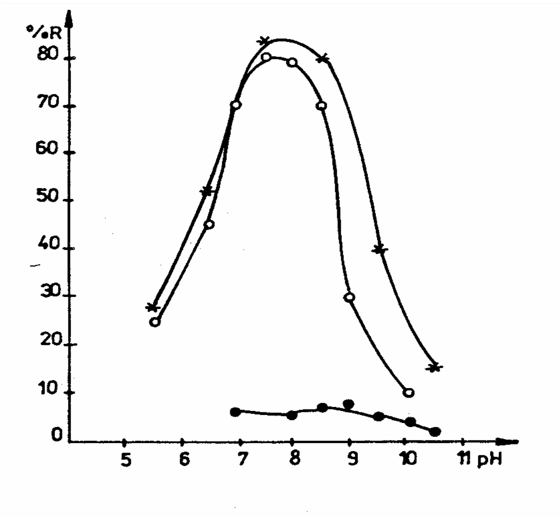


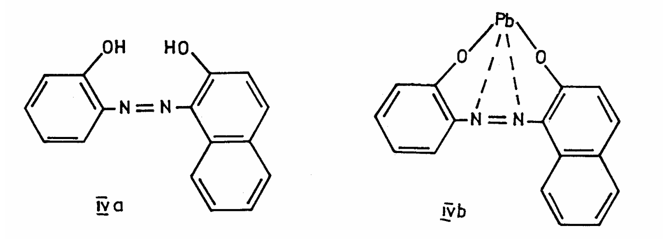
Figure 7. The variation of %R depending on the pH with 0,5 g/l acetylacetone and
0,1 g/l isooctane for:

✱ galene
o ceruzite
● calcite.

It can be noticed that galene and ceruzite float well maximum recuperations of 84% for galene and 80% for ceruzite at pH = 7,5 being realised. The result obtained is in contradiction with the small stability of the chelates Pb (II) with acetylacetone in solution.

2 hydroxyphenyl azonaphtol 2

This reagent presents the structure IVa and forms with Pb (II) a chelat compound with the structure IVb.



The chelat compound formed in solution has a maximum stability for the pH between 7 and 10, as shown in figure 8.

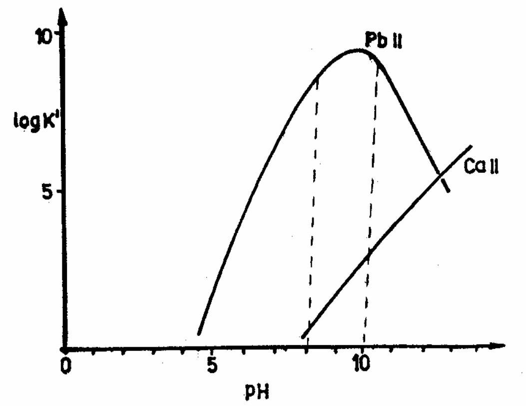


Figure 8. The variation log K'' with the pH for the compounds formed by 2 hydroxy-phenyl azonaphtol with Pb (II) and Ca (II).

The solution tested for flotation gives sufficient foam without isooctane. The pH used was between 6 and 9,5.The results presented in figure 9 show that the maximum recoveries are 68% for galene and 64% for ceruzite both for pH = 7,5. Calcite floats little, only 14%, for pH = 9,5.

The results obtained are in concordance with the foresights deducted from the data of analitical chemistry.

2 hydroxytrimethylenediaminotetraacetic acid

The reagent presents the structure Va and forms stable compounds with Pb (II) in solution with the structure Vb,for pH between 7 and 10, as shown in figure 10.

This solution does not float ceruzite and galene in contradiction with the pretty high stability of the Pb (II) chelat compounds in solution.

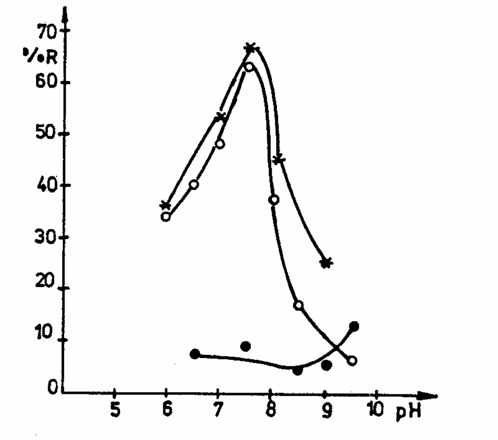
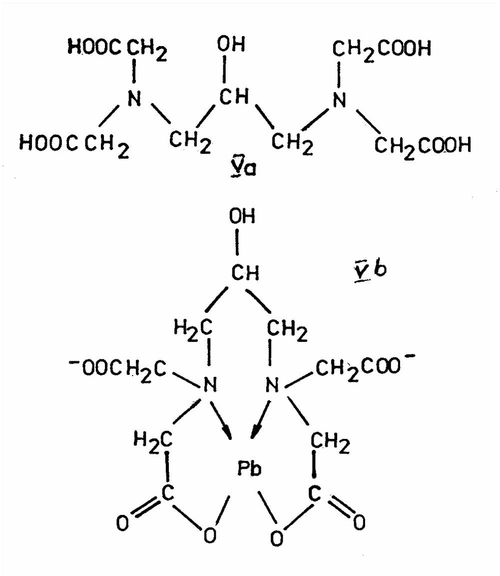


Figure 9. The variation of %R depending on the pH with 0,023 g/l 2 hydroxyphenyl azonaphtol 2 for:
✱ galene
o ceruzite
● calcite.



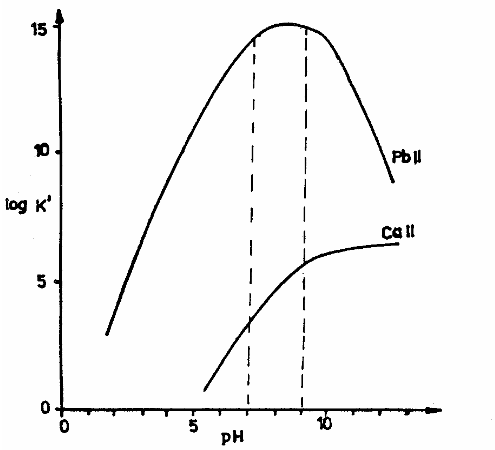


Figure 10. The variation log K' with the pH for the compounds formed by 2 hydroxy trimethyl-enediamino-tetraacetic acid with Pb (II) and Ca (II).

The spectra I.R. for the system 8 - hydroxyquinoline - ceruzite

In figure 11 are reunited the spectra I.R. for pure ceruzite, curve (a), Pb (II) oxinate, curve (b) and ceruzite after the treatement with oxyne solution in acetone with pH = 9, curve (c), respectively. By comparing the spectres we can notice the presence of bands characteristic to the Pb (II) oxynate from 1320, 1280, 1110, 865, 728 cm^{-1} in the spectre of ceruzite treated with 8 - hydroxyquinoline. Therefore on the surface of ceruzite treated with the solution of reagent with chelatant action is formed the Pb (II) oxynate.

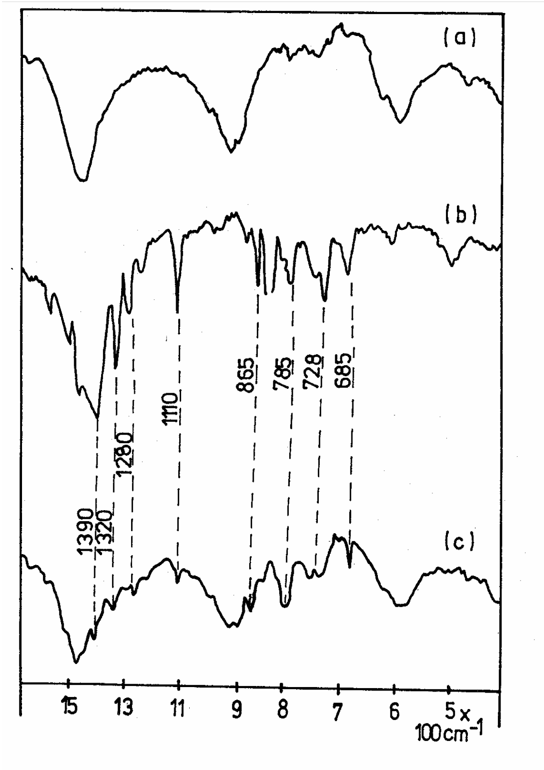


Figure 11. The I.R. spectra indicating the adsorbtion of oxyne onto ceruzite a) ceruzite in KBr b) Pb (II) oxynate c) ceruzite after treatment with acetone solution of oxyne.

CONCLUSIONS

8- hydroxyquinoline floats well galene and ceruzite and the maximum recoveries takes place in a pH domain where the stability of the chelat complexes formed is also maximum, the collector system must contain both oxyne and diesel oil, because oxyne forms along with the cation Pb (II) on the surface of the mineral insoluble metallic chelats to which diesel oil adheres by physical adsorbtion, ensuring the hydrophobization of the mineral.

Eriochrome black T in the presence of isooctane and ***2 hydroxyphenyl azonaphtol 2*** in the absence of isooctane float well galene and ceruzite, the results being in concordance with the foresights deducted from the data of analitical chemistry referring to the apparent constant of complexation and the pH domain for chelats formed with Pb (II) in solution.

Acetylacetone floats well galene and ceruzite in the presence of isooctane, in contradiction with the small stability of the Pb (II) chelats with this reagent in solution.

2 hydroxytrimethilenediaminotetraacetic acid forms stabile compounds with Pb (II) in solution but it does not float the analysed minerales.

Calcite floats very little with the mentioned reagents.

For the reagents 8 - hydroxyquinoline, eriochrome black T, 2 hydroxyphenyl azonaphtol 2 and acetylacetone, the achieved recoveries for ceruzite (Pb (II) oxidized mineral) are comparable to those achived for galena (sulphure). Thus, by using a reagent with chelatant action we can remove the barrier between the sulphuric non-ferrous minerals and the oxidical ones which do not behave identically under the action of the same conventional collector.

The I.R. spectra analysed in the present work give evidence of the formation of Pb(II) oxinate on the surface of ceruzite during the flotation process in which 8-hydroxyquinoline is used as a collector. This evidence is supported by the numerous bands belonging to Pb (II) oxynate in the I.R. spectrum of ceruzite treated with the reagent with chelatant action.

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