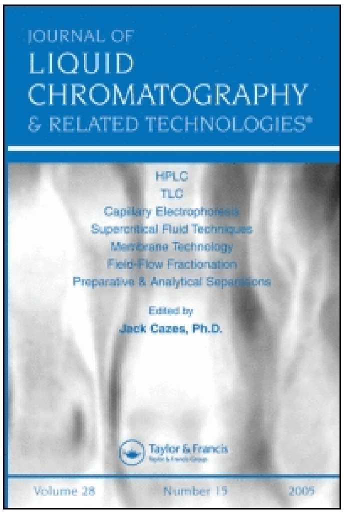

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OPTIMIZING MODIFICATION CONDITIONS OF SILICA GEL WITH METAL SALTS

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ABSTRACT

In this study, the trial of optimising modification conditions of silica gel with metal salts was undertaken. For the purposes of the study, colourful salts Cu(I), Cu(II), Co(III) were mainly chosen, which enabled the evenness of the coating and the effectiveness of their desorption.

Among many techniques of impregnation, impregnation by dipping and developing of the commercial plates Kieselgel $60F_{254}$ and hand-made plates from the suspension of silica gel in salt solution ($ZnCl_2$) was chosen. The absolute concentration of a metal on the layer was measured using Atomic Absorption Spectrometry (ASA) method. On the plates impregnated by developing, the demixion front was observed, the height of which depended on the concentration of the developing solution.

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Beneath the front, independently of its height, the saturation of silanol groups was constant and reached approximately 7%. In the case of impregnation by dipping, the impact of the dipping period, the concentration of the external solution and its pH, on the quantity of the adsorbed metal ions were all studied.

The analysis of a wide spectrum of salt concentrations in the external solution revealed the existence of the centres on silica gel surface, differentiated in their ability for ion-exchange adsorption. The most reactive centres, constituting about 7% of all silanol population, provide ion bonding of a metal which was confirmed by EPR analysis.

The study of the modified silica gel structure was also supplemented by the pictures from a scanning electron microscope.

INTRODUCTION

Adsorbents impregnated with metal-ions, mainly from the transient groups, are used in the Thin-Layer Chromatography (TLC) of the compounds which possess the electrono-donor groups, as amines, hydroxyamines, mercaptants, sulphides, amino-acids, and others.[1-4] These compounds are characterised by the ability to form complexes with metals which, in turn, makes it possible to differentiate their retentions.

There are many studies on the separation of aminoacids and their derivatives. These compounds were analysed on the adsorbents modified with Cu(II), Cd(II), Zn(II), Mg(II), Fe(II), Co(II), Ni(II), Mn(II) and other metal ions. Sulphonamides were also successfully separated by TLC on the adsorbents impregnated with Cd(II), Zn(II), Mn(II), Co(II), Cr(III), Fe(III).[5-7]

An important group, among these types of stationary phases, is constituted by the adsorbents impregnated with silver ions which display great selectivity in relation to the non-saturated compounds. This, so called, "argentation TLC" based on the ability of silver ions to create π-complexes with the non-saturated ligands, found its application mostly in the analysis of the lipids, their separation and examining of their structure.[8,9]

The process of impregnation with metals is most often carried out on silica gel, florisil, polyamide supplemented with various techniques like salt addition to the suspension of different adsorbents, dipping, or spraying with salt solution. It is mainly silica gel that has become the subject of a more detailed investigation concerning metal additions. It is already known that these metal additions can occupy three main positions in gel structure, secluded, internal, and surface.[10]

The first group, deeply hidden in the silica structure, does not influence chromatographic parameters. The second group are metal traces of barium, aluminium, or magnesium which being close to the gel surface are responsible for the creation of the so called “structural centers of Lewis” which influence the increase in neighbouring silanol groups acidity. The existence of metal impurities is visible in the substantial increase of silica acidity, which undergoes deprotonisation at the lower pH values (3.0 – 9.0) in comparison with the higher values (7.5-9.0) in the absence of metal additions. The last group of metal additions are metal traces on the surface layer. These metals change the character of active centres on gel surface, thanks to their free orbitals capable of creating complex links with solvent molecules and separated compounds during the chromatographic process. They can be easily introduced onto the surface, taking advantage of an ion-exchange character of silanol groups and easily gotten rid of by extraction with an acid or EDTA solution.

$$n-\mathrm{Si}-\mathrm{OH}+\mathrm{Me}^{+m} \rightleftarrows (\mathrm{Si}-\mathrm{O})_m\,\mathrm{Me}+n\mathrm{H}^+$$

In chromatographic analysis on stationary phases obtained by metal impregnation most controversies evolve around establishing the salt concentration value in the stationary phase. In the studies devoted to Ag–TLC the following recommendations have been proposed: the application of $AgNO_3$ solution from 5% up to 30% for preparing the adsorbent suspensions, 0.3 – 0.4% for the impregnation by dipping and 10 – 20% $AgNO_3$ solution for plate spraying.[11]

In the literature available there are many reports on practical issues, however there is a considerable lack of reports devoted to optimising modification conditions of the chromatographic adsorbents with metal salts. The aim of the study was to trace the rules that might serve as the basis for the rational choice of a method and impregnation conditions.

EXPERIMENTAL

Modification of Commercial Silica Gel Plates

Silica gel layers: Kieselgel $60F_{254}$ (10×10 cm) plates from E. Merck (Darmstadt, Germany) were washed with methanol overnight in a normal chromatographic chamber before being impregnated. The plates were developed in Chromdes (Lublin, Poland) horizontal sandwich DS-chamber with aqueous salt ($CuSO_4$) solution at various concentrations. The impregnation by dipping was conducted in a glass vessel, by the immersion of the plates in the salt solution (50 mL).

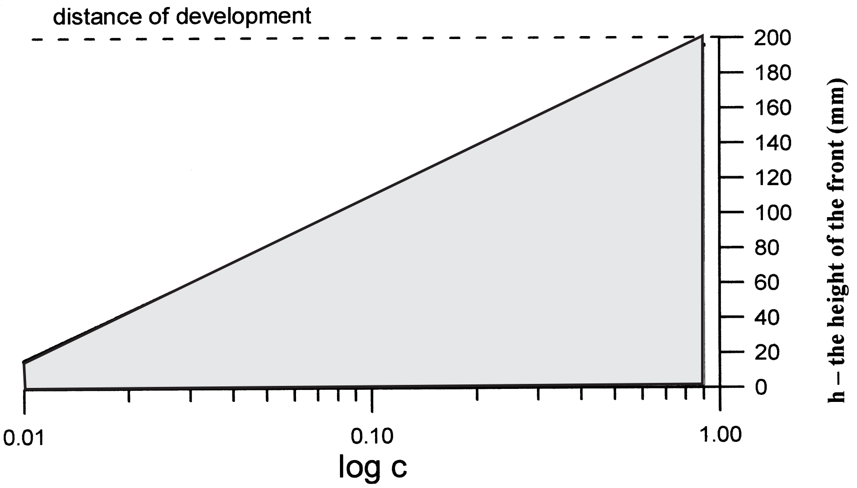


Figure 1. Correlation between the height of the front (h) and the logarithm of the ($CuSO_4$) mole salt concentration in the developing solution (c).

After dipping, the plates were placed for a few seconds in distilled water to get rid of the salt excess. The plates were dried, heated in a drying cabinet for ca 1 h at 110°C and after cooling, scraped and eluted with 1 M hydrochloric acid. At least three plates were developed for each measurement. In the eluate, the metal content was determined by ASA method.

Modification of the Hand-Made Silica Gel Plates

Modified plates were obtained by preparing the suspension of Kieselgel $60F_{254}$ (Merck) in aqueous solution of salt $ZnCl_2$ (Merck). They were dried in air for 30 minutes and activated at 120°C for 2 hours. 2 μL solutions (0.2%) of aniline derivatives in anhydrous ethanol were spotted 1 cm from the edges of the plates which were then developed to a 18 cm distance. The spots were detected under UV illumination ($\lambda = 254$ nm). The dependence of the quantity of the adsorbed metal ions upon pH was investigated by shaking 5 g of silica gel with the 100 mL $1{\cdot}10^{-2}$ $mol{\cdot}l^{-1}$ Cu_2Cl_2 solution, $2{\cdot}10^{-2}$ $mol{\cdot}l^{-1}$ $CuSO_4$, or $2{\cdot}10^{-2}$ Co(III) solution. Co(III) was a product of oxidation Co(II).[12] The suspension was brought to a required pH with the ammonia solution (3 M). After a 15 minute shaking the excess of impregnation solution was washed off by filtration using distilled water. The adsorbed complex was eluted with 1 M HCl. In the extract, the metal content was determined by the ASA method.

Apparatus and Measurement Conditions

Scanning of the chromatograms was performed by transmission densitometry at $\lambda = 800$ nm using a Camag Scanner 3 densitometer. The pictures were produced using scanning microscopy BES 300 (Tesla).

The silica gel samples were impregnated with 0.005 and 0.2 M $CuSO_4$ solution for the period of 1 h, analysed on EPR spectrometer in range X (app. 9.5 GHz) connected to a computer, in the range of magnetic field values from 10 – 1000 mT (100 – 10 000 G). The measurements were performed in quartz samples. The spectra were elaborated by using Origin 3,5 programme. The metal content was determined by the use of Pye-UnicamSP 192 Atomic Absorption Spectrometer.

RESULTS AND DISCUSSION

Modification of Commercial Silica Plates by Development and Dipping

The development of a silica gel plate with $CuSO_4$ solution causes the rise of a concentration gradient of a metal ion, which is observed as a demixion front. The height of the front depends on the concentration of a salt applied.

The existence of directly proportional dependence between the height of the front (h) and the logarithm of the salt concentration in the developing solution (c) was empirically proved. The plot presenting the function course h = f (log c) was shown in Figure 1.

As the increase of the developing solution concentration leads to some disturbances in the course of the demixion front, uniform coating of the whole surface by the single development is not possible. This could, however, be achieved by the method of continuous development with the solution of medial concentration in the open chamber with the simultaneous sucking of the developing solution.

The quantitative examination by ASA pointed out that independently of the front height and the development method applied, the surface excess amount occurring at the phases border presents a fixed value and corresponds approximately to $2 \cdot 10^{-4}$ Cu^{2+} mol/g of an adsorbent which, taking into account the average number of OH groups on the surface, provides the saturation of about 7% (Table 1).

For the purpose of optimising impregnation conditions of the commercial silica plates by the dipping method, the investigation of the quantity of the Cu^{2+} adsorbed ions depending on the dipping time and the concentration of external solution ($CuSO_4$) was performed.

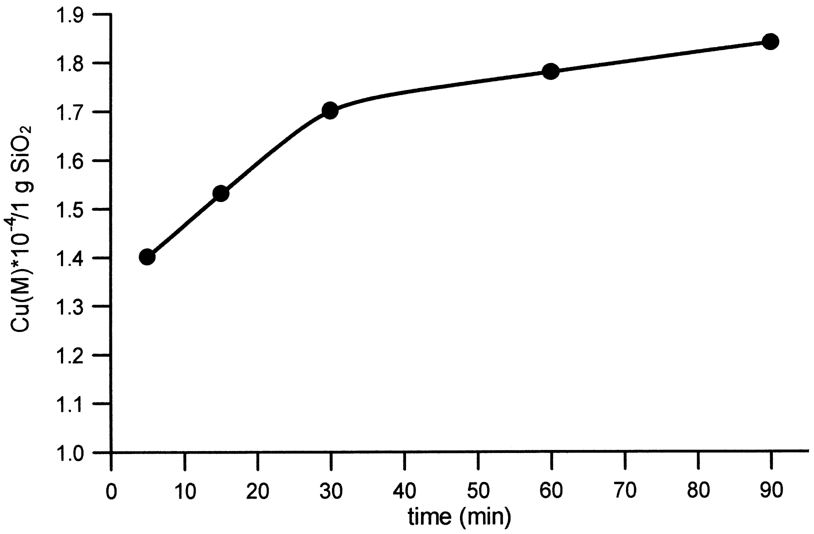


Figure 2. Correlation between the amount of Cu moles adsorbed per 1 g silica gel vs. impregnation time.

Table 1

Correlation Between Amount of Cu(II) Adsorption per 1 g Silica Gel vs. Concentration of Developing Solution ($CuSO_4$)

Mole Concentration of the Developing Solution ($CuSO_4$)	Amount of Mole Cu(II) adsorption per 1 g of Silica	Ratio of Mole No. Reacting with Cu(II) to the Total No. of OH Surface Groups	Percent of Saturation of Silanol Groups
0.02	$1.80 \cdot 10^{-4}$	0.13	6.46
0.04	$1.83 \cdot 10^{-4}$	0.13	6.57
0.08	$2.11 \cdot 10^{-4}$	0.15	7.57
0.10	$2.08 \cdot 10^{-4}$	0.14	7.47
Continuous development with 0.04 M ($CuSO_4$) solution	$1.86 \cdot 10^{-4}$	0.13	6.68

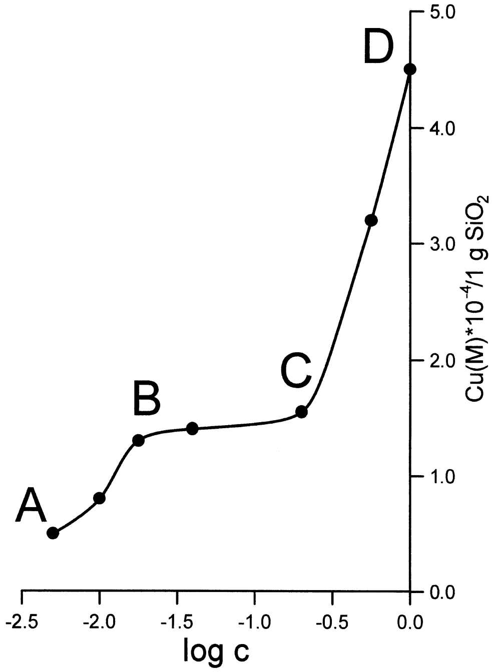
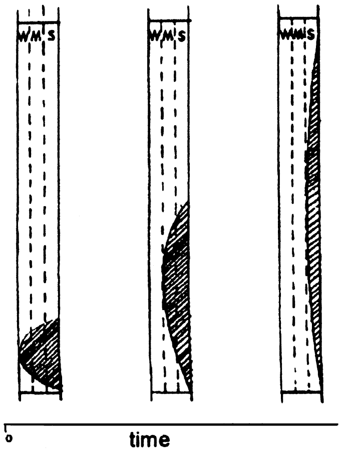


Figure 3. Correlation between amount of Cu moles adsorbed per 1 g silica gel vs. log(c) (c – mol concentration of aqueous $CuSO_4$ used for impregnation).

The results obtained for different periods with horizontal dipping technique are illustrated at Figure 2. Following that plot, one may explicitly state that in the static system, the process of ion-exchange occurring on the border surface of an adsorbent and – the external solution reaches equilibrium of the dynamic state in 1 hour. This equilibrium is consistent with the law of mass action or with the equations of adsorption isotherm of Freundlich, Langmuir's and other related dependences characterising adsorption at the limited volume of an adsorption layer.

As for examining the dependence between the concentration of the impregnating solution and the mole number of metal ions (Cu) undergoing adsorption, a wide concentration spectrum of the external solution of $CuSO_4$, from 0.005 M to 1 M, was applied, which allowed a detailed tracing of the adsorption kinetics of Cu^{2+} ions on the silica gel. The plot obtained (Figure 3), presenting the quantity of the adsorbed Cu^{2+} moles on 1 g of gel in the logarithm function from the concentration of an impregnating solution, is a straight line having two flexion points (B and C). Its course points to big analogies to gas-phase titration, which differentiates the spots on the gel surface with respect to



Scheme 1. The sequence of the engaging of the sites differentiared by the force of adsorption interactions on the surface of silica gel.[13]

their adsorption reaction force.[14] In this method, by analysing the influence of various amine quantities on the retention time of an aromatic hydrocarbon (benzene), it was shown that the dependence plot of the relative decrease of its retention in the amine concentration function is also a straight line with two flexion points. The values of amine concentration in these points corresponded to the concentrations of the strongly interacting adsorption centres on the gel surface.

The course of the plot presented in Figure 3 also suggests the existence of the sites varied according to their interactive, exchanging force. The AB part corresponds to the reaction of strong sites (S) taken first, according to Scheme 1.

Considering ion adsorption value in point B ($1.27 \cdot 10^{-4}$ mol/g), the relation of the reacting substrates (2:1) in accordance with surface reaction of silica gel, one may conclude that the silica gel examined contained active centres of 0.6 μmol/m^2 concentration. Assuming that fully hydrolysed silica contains 8 μmol–OH/m^2, this group constitutes about 7% of the total silanols' count. The existence of this small population of very active silanols on the silica gel surface has been mentioned many times in the literature. This phenomenon was also investigated by Sadek who based his examination on studying metal impurities in the silica structure.[10] It is well visible that their quantity may be different depending mainly on the kind of gel used. It ranges from 1.5 to 13%, while the gels used for HPLC contain about 5%[14] of reactive silanols up to GC of about 0.3%.[15]

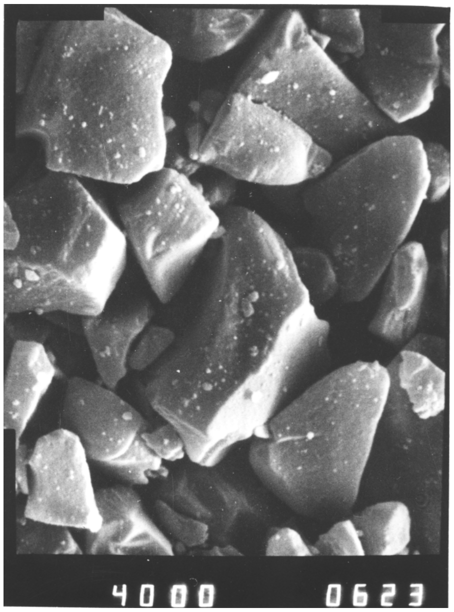


Figure 4. Scanning electron micrographs of Kieselgel Si $60F_{254}$. Enlargement 4000×.

The BC part pictures medium strength (M) centres, which come into existence with an increase of the external solution concentration. The last part – CD, describes the alignment of weakly adsorbing centres on the silica gel surface (W).

Further investigation of the dependence which was initiated by the minimal, border salt concentration (0.005 M.) stabilising the adsorbent surface in aqueous solution was impossible to be continued because of the limited solubility of $CuSO_4$ in H_2O (20.7 g/100 ml H_2O).

Part of the plot (Figure 3) – that is ABC part – has a typical form of an adsorption isotherm of the solid from the solution, however with approaching the limit of its solubility, the value of adsorption rapidly increases and tends asymptotically to the line parallel to the adsorption axis. In such a broad concentration range of the impregnating solution, ABCD plot looks like the excess adsorption isotherm of binary solutions of liquids of limited miscibility. Rapid adsorption increase, at the concentrations close to saturation, suggests that under the influence of the porous structure of an adsorbent, premature salt crystallisation occurs. It is confirmed by the microscopic studies performed on a scanning electron microscopy (SEM) (Figures 4, 5).

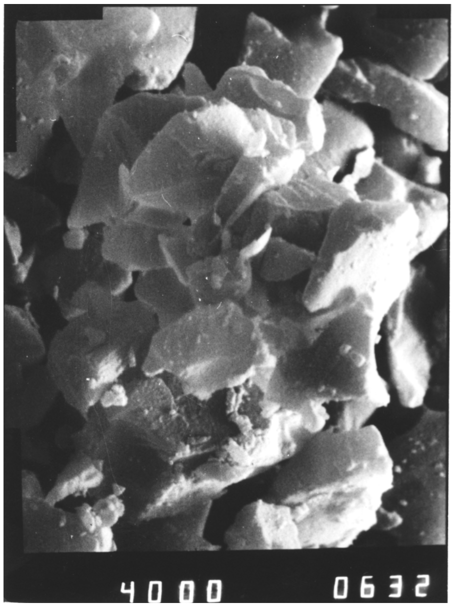


Figure 5. Scanning electron micrographs of silica gel plate impregnation of 0.5 M $CuSO_4$. Enlargement 4000×.

Thanks to high-resolution of SEM, by comparing the photographs, one may easily notice salt crystals "enclosing" the particles of silica gel. Another proof comes from the EPR spectra which display the exchanging reactions between silanol groups and copper ions in given impregnating conditions. The spectral form additionally suggests the possibility of coordinating Cu(II) ions by the siloxal bridges of the silica gel (Figure 6).

The Influence of the pH of an Impregnating Solution on the Concentration of the Adsorbed Metal Quantities

In the pH range examined (4 – 8), the silica gel plays the cation-exchanging part.[16] The increase of pH over 9 would cause deprotonisation of silanol groups with a partial dissolving of the silica.

As the process of ion-exchange described by the equation[1] is reversible in the acidic solution, there exists a clear dependence of the ion-exchanging ability on the pH of the external solution. This dependence is illustrated in Figure 7.

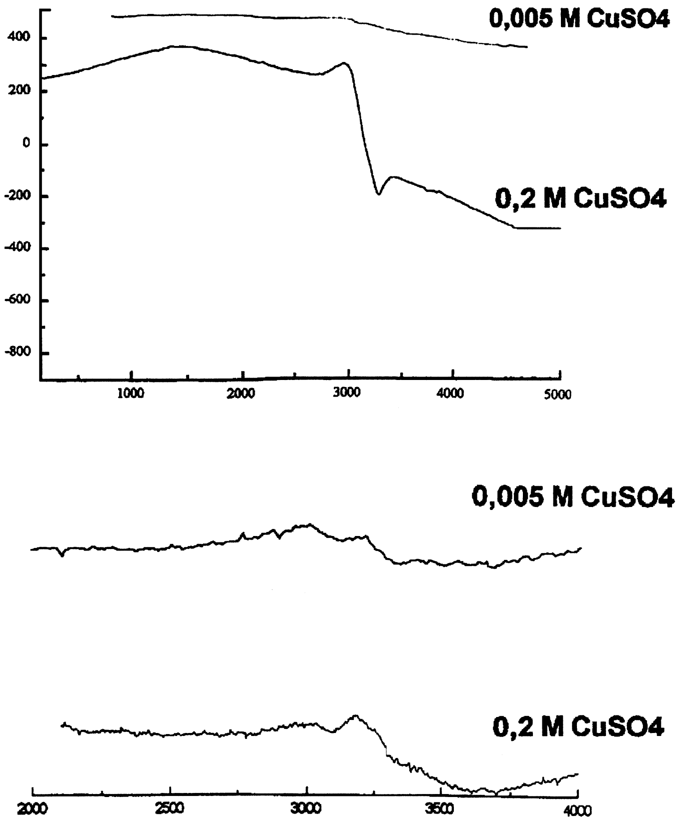


Figure 6. EPR spectra of silica gel plates Kieselgel Si $60F_{254}$ impregnated by 0.005 M and 0.2 M $CuSO_4$ for 1 hour.

The course of the plots is determined by the pH influence on the dissociation of the active groups of the sorbent as well as by the presence of the competitive ions in the solution (H^+, OH^-). Moreover, pH influences not only the character of the silanol groups but also the hydrolysis of the ions of transient elements discussed.

Vydra et al.[17] noticed that for the cations undergoing hydrolysis, the sorption coefficient increases when pH increases. This was already noticed by Djurfeldt and Samuelson[18] in the 1950s when they observed the increase of the ion-exchange ability of the cation-exchangers with some metals (Fe^{3+}, for example), which was caused by the adsorption of their hydrolysed form.

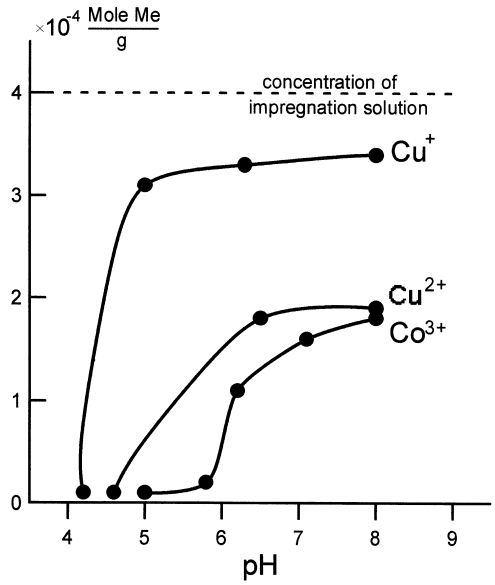


Figure 7. Dependence of pH of the external solution Cu(I), Cu(II), Co(III) upon values of their adsorption.

That is why the influence of pH on dissociation degree of silanol groups and the hydrolysis of the metal-ions mentioned, makes the whole process of ion-exchanging on the silica gel in electrolytes' solutions quite a complex problem. A summary effect of the phenomena described, is a large increase of adsorption of Cu(I), Cu(II) ions in the picture with an increasing pH, which for pH ≈ 4 is 17018 ppm Cu(I) and 3302 ppm Cu(II), and pH ≈ 8 – 12190 ppm for Cu^{2+} and almost two times more – 22500 ppm for Cu(I).

The maximum quantity of an adsorbed ion is, then, proportional to the value of the electrical potential, which proves the fact that the reaction is a stechiometric process. A quite different plot course was achieved for Co(III) ions.

Two times higher than expected maximum adsorption of these ions is probably caused by the creation of two-core complexes of Co(II) with ammonia which undergos cyclization with the creation of peroxide bridges (see scheme 2).[12] The curve form is different from the curves for Cu(II) and Cu(I) which were close in their form to Langmuir's isotherms.

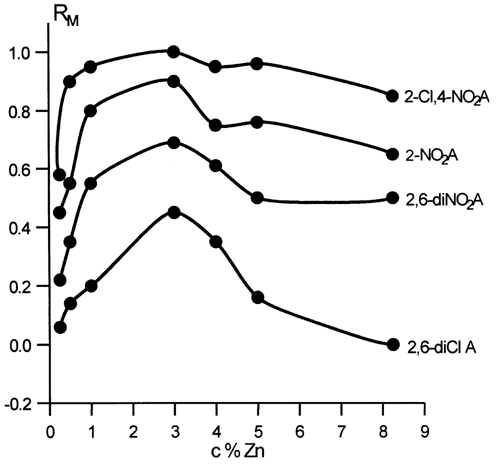
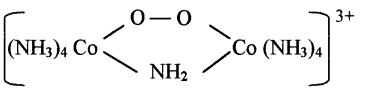


Figure 8. Plots of correlation R_M values vs. concentration of metal ions (Zn(II)) in stationary phase for aniline derivatives (A). Eluent 5% propanol-2 in heptane.



Scheme 2. The structure of Co(II) complex in the ammonia solution.

Metal-Ion Concentration in the Suspension of Silica Gel

An optimal concentration of a metal ion in the suspension of the silica gel was chosen on the basis of the chromatographic analysis, that is the retention data of model compounds on the adsorbents containing different concentrations of metal ion.

The measurements performed on the modified adsorbents in the broad range of concentrations, that is from 0.25 – 8.25% (Figure 8) enables tracing, in full detail, the influence of an impregnating ion on the chromatographic parameters.

The metal-ion (Zn) content in the adsorbent suspension which ranges from 78.7 μmol/g to 0.946 mmol/g is connected with the retention increase for all analysed compounds.

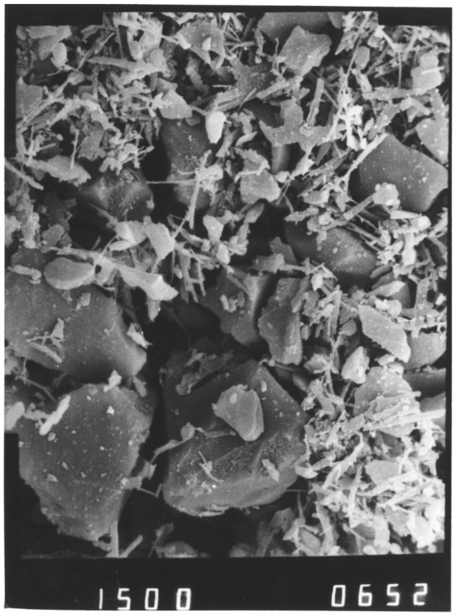


Figure 9. Scanning electron micrographs of silica gel prepared from the suspension of SiO_2 in 5% aqueous solution of $ZnCl_2$. Enlargement 4000×.

The maximum retention value was acquired for an adsorbent, the hydroxyl groups of which were saturated in 32.3%. Further increase in concentration caused the minimal decrease in retention, probably due to the creation of polar coordination complexes of the analysed compounds with the metal ion in the mobile phase. This hypothesis is confirmed by the photograph of the modified silica gel, prepared from the suspension of SiO_2 in 5% solution of $ZnCl_2$, where the excess of salt is visible as the minute crystals (Figure 9).

These crystals have the possibility of dissolving in the mobile phase and by the same time they determine the occurrence of the mechanism characteristic of the chromatography of complexes.

CONCLUSION

Impregnation of silica gel with metal salts gives the possibility of obtaining new selective stationary phases. With regard to an easy process of acquisition and a great variety, acquired by changing the kind of metal ions used, these phases have a great chance to become a more popular adsorbent in TLC.

The full characteristics (qualitative and quantitative) of the modified silica gel was possible thanks to quantitative examinations (ASA), spectroscopic examination (EPR) and microscopic analysis.

The picture of the structures obtained in this way, which is crucial for all separation methods may ease the identification of the mechanisms which rule the retention on stationary phases of this type in future studies. The analysis of a few compounds of an electrono-donor character on silica gel modified with Zn(II) ions presented above, suggests that not only the ion kind but also its concentration may constitute a method in optimising separation in this chromatographic technique. The choice of the metal concentration in the adsorbent layer will also decide the retention mechanism and will allow a fuller interpretation of the obtained results.

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