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**Microdetection of Some Biologically Active Thiol
Compounds with Sodium Pentacyanoammineferrate(II)
on Ion-Exchange Resin Grains**

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A new test for microdetection of thiol compounds, using sodium pentacyanoammineferrate(II) as a reagent and ion-exchange resin as the reaction medium, is presented. Nineteen thiol compounds were examined, some of them known and used as biologically active substances. Detection limits and tolerance limits were investigated. Limits of concentration, limits of dilution and exponents of sensitivity were evaluated.

INTRODUCTION

The »resin spot test« is a micro- or ultramicro-detection technique that uses tiny grains of an ion exchanger as the reaction medium.^{1,2} Recently we worked out microdetection procedures for the following substances: uranium,³ silver,⁴ biologically significant metals,⁵ ketones,⁶ nitroso compounds,⁷ barbiturates,⁸ and hydroxamic acid⁹ using the resin spot test technique.

Pentacyanoammineferrate(II) ions, AmPF, react with various organic compounds containing sulphur,¹⁰⁻¹⁴ forming intensively coloured, mostly substitutional complexes. The complexes are produced via the pentacyanoaquoferrate(II) ion, which is formed as an intermediate in aqueous AmPF solutions.^{15,16} We worked out a simple test for the microdetection of such compounds based on the sorption of the coloured complexes, formed with AmPF as a reagent, on a strongly basic ion exchanger.

EXPERIMENTAL

Chemicals and Solutions

All the chemicals used were of »analytical grade«.

Sodium pentacyanoammineferrate(II), AmPF, (Touzart-Matignon, France). A 0.2% (w/v) aqueous solution was freshly prepared before use.

Acetate buffer 0.2 M, pH = 4.6 (E. Merck, DR).

Amberlite IRA-401, strongly basic anion exchange resin, Cl-form, effective size 0.40—0.50 mm (Rhom and Haas Co., USA).

The examined thiol compounds (obtained from commercial sources) were dissolved to a concentration of 2 mg·ml⁻¹ in water or in 96% (v/v) ethanol. Due to the limited solubilities and some other properties, the concentration of dimercaprol solution was 2.24 mg·ml⁻¹, thioglycollic acid 3.42 mg·ml⁻¹, and *p*-dimethylaminobenzilidene-rhodanine 0.5 mg·ml⁻¹.

Apparatus

Dropping capillary pipettes. Only tested glass capillary pipettes delivering a drop of water of 0.3 ± 0.001 ml were used.

Procedure

Several grains of Amberlite IRA-401 (Cl-form) were placed on a white Feigl plate. 1 drop of AmPF reagent solution, 1 drop of the sample solution, and 1 drop of acetate buffer were added and the mixture was stirred. The colour that developed after 1 minute on the resin grains was compared with an appropriate reagent blank. Thiol compounds gave differently coloured grains (see Table I).

TABLE I

Resin Spot Test Results. Characteristics of Detection, Detection Limit (LI), Concentration Limit (LC), Dilution Limit (LD) and Exponent of Sensitivity (pD)

Thiol compound	Colour	LI(μg)	LC(g·ml ⁻¹)	LD(ml·g ⁻¹)	pD
Cysteine Hydrochloride	light green	50	1.00×10^{-3}	1.00×10^3	3.00
Dimercaprol	green	50	1.00×10^{-3}	1.00×10^3	3.00
Mercaptosuccinic Acid	purple	10	2.00×10^{-4}	5.00×10^3	3.70
Thioglycollic Acid	light green	10	2.00×10^{-4}	5.00×10^3	3.70
Potassium Xanthogenate	bluish-green	1.0	2.00×10^{-5}	5.00×10^4	4.70
Sodium Diethyldithiocarbamate	brownish-green	25	5.00×10^{-4}	2.00×10^3	3.30
Rubeanic Acid*	blue	3.0	6.00×10^{-5}	1.67×10^4	4.22
Thioacetamide	brownish-red	0.1	2.00×10^{-6}	5.00×10^5	5.70
Thiosemicarbazide	violet	1.0	2.00×10^{-5}	5.00×10^4	4.70
Thiourea	blue	0.5	1.00×10^{-5}	1.00×10^5	5.00
6-Mercaptopurine*	green	4.0	8.00×10^{-5}	1.25×10^4	4.10
2-Mercaptopyridine	light green	1.0	2.00×10^{-5}	5.00×10^4	4.70
Thiamazole	bluish-violet	1.0	2.00×10^{-5}	5.00×10^4	4.70
Thionalide*	green	50	1.00×10^{-3}	1.00×10^3	3.00
Thiosalicylic Acid*	bluish-green	25	5.00×10^{-4}	2.00×10^3	3.30
3,4-Dimercaptotoluene	green	30	6.00×10^{-4}	1.67×10^3	3.22
<i>p</i> -Dimethylaminobenzilidenerhodanine*	green	3.0	6.00×10^{-5}	1.67×10^4	4.22
Ethionamide*	bluish-violet	1.5	3.00×10^{-5}	3.33×10^4	4.52
Thiopentone*	pink	3.0	6.00×10^{-5}	1.67×10^4	4.22

* dissolved in 96% ethanol

RESULTS AND DISCUSSION

All the investigated thiol compounds yield water soluble, intensively colored complexes with AmPF on a resin grain phase. To establish optimal working conditions we examined the influence of the following factors: concentration of the reagent, type of the ion exchange resin, pH of the medium, and sequence of reactant addition.

The optimal reagent concentration was found to be 0.2% (w/v). Higher concentrations were not suitable because they only increased the coloration

of the resin grains in the reagent blanks, but had no influence on complex formation.

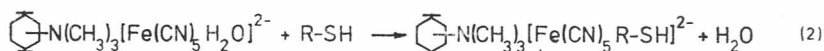
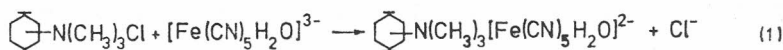
The sorption of the complex onto the grains was examined on eleven ion exchange resins (Amberlite IR-120, IRC-50, IRA-400, IRA-401, IRA-410, IRA-68, and IRA-45; Dowex HCR, and 2-x8; Lewatit CNP, and MP-62). It was found that the maximal sorption of coloured products occurred when the strongly basic anion-exchange resin Amberlite IRA-401 was used.

The pH of the medium had a significant influence on complex formation, specifically on the following parameters: the colour of the complex, its intensity, and rate of sorption. The best results were obtained in weakly acidic medium, and therefore acetate buffer (pH = 4.6) was added to the reaction mixture.

The reactant sequence is also important; the AmPF must be fixed on the resin grains prior to addition of sample and buffer addition [see Equation (1)].

This microdetection test has to be performed at room temperature, because elevated temperature causes reagent decomposition. Limits of detection, concentration, dilution, and exponents of sensitivity (pD) are listed in Table I for several thiol compounds and some similar substances.

In the first step of the reaction, the reagent AmPF is adsorbed onto the resin grains and then follows the formation of the coloured complex with analyte. Among organic compounds containing sulphur these coloured complexes result only with thiol compounds, or substances containing a C=S group which can easily become a C-SH group. The color of the adsorbed products is mostly green, rarely blue, violet or red. On the basis of the results obtained in this study, as well as on the basis of literature data,¹⁴ the reaction scheme for the resin spot test technique might be:



A number of foreign substances (alcohols, aldehydes, amides, amines, amino acids, azo compounds, carboxylic acids, esters, hidrazides, hydrazines, ketones, nitro compounds, nitroso compounds, phenols, and sulphonic acids) were examined and found not to interfere. Some organic compounds do not interfere providing that the tolerance limit is observed. The values of tolerance limit for typical organic substances are presented in Table II.

TABLE II
Tolerance Limit for the Detection of 5 µg Thiocarbamide (Thiourea)

Tolerance limit (µg)	Substance added
50	<i>p</i> -dimethylaminoazobenzene, <i>p</i> -toluenesulfonyl hydrozine
10	acetylhydrazide, phenylhydrazine, alizarinsulfonic acid
1	pyrogallol isoniazid

According to the values of the tolerance limit (Table II) detection of thiol compounds is most frequently interfered by hydrazines and hydrazides. Tolerance limits for other studied analytes (Table I) are similar to those obtained for thiourea. These values are also in agreement with previously published results for mercaptans using sodium-pentacyanonitrozilferate(II) as a reagent.¹⁷

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SAŽETAK

Mikrodokazivanje nekih biološki aktivnih tiola s natrij-pentacijanoaminoferatom(II) na zncima ionsko-izmjenjivačke smole

V. Grdinić i M. Jakševac-Mikša

Predložen je novi postupak za mikrodokazivanje tiola koji se provodi na zncima Amberlite IRA-401 (Cl-oblik) uz natrij-pentacijanoaminoferat(II) kao reagens. Konačni produkti reakcije na zncima ionskog izmjenjivača različito su obojeni, što pospješuje identifikaciju pojedinačnih supstancija. Određene su granice dokazivanja (0,1—50,0 µg) i procijenjene ostale granične vrijednosti kvalitativnog ispitivanja. Alkoholi, aldehidi, amidi, amini, aminokiseline, azo-spojevi, karboksilne kiseline, esteri, hidrazidi, hidrazini, ketoni, nitro-spojevi, nitro-rozo-spojevi, fenoli i sulfonske kiseline ne ometaju dokazivanje tiola, a nekim supstancijama je utvrđena granica tolerancije. Ispitano je 19 tiola od kojih su neki biološki aktivne supstancije.