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Colorimetric sensor for determination of thiocyanate in fossil and drill waters

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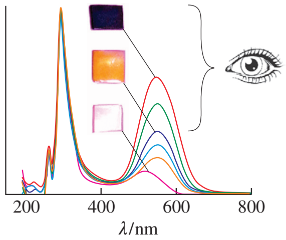
A colorimetric sensor is proposed for determination of thiocyanate based on the destruction of mercury–diphenylcarbazone complex immobilized in the optically transparent polymethacrylate matrix in the concentration range 0.8–50 mg dm^{-3} with the detection limit of 0.6 mg dm^{-3} or visual determination with ‘naked eye’ in the concentration above 1 mg dm^{-3}. The possibility of application of such sensors for determining thiocyanate in fossil and drill waters is shown.



The quantification of contamination through drilling procedures may be essential for the scientific interpretation of chemical data on groundwaters obtained from drilled monitoring wells. Thiocyanate ion can be a suitable chemical agent to track the distribution of drilling fluid during well drilling.[1] Reagents of different types are used for determination of thiocyanate. Pyridine–pyrazolone, pyridine–benzidine, pyridine–sulfonyl methods of detecting thiocyanate ions through its oxidation and subsequent interaction with pyridine in the presence of additional substances are the most studied tools.[2] One of the most sensitive and useful methods of detection of small amounts of thiocyanate is the conversion of thiocyanate ions upon the treament with active chlorine into the chlorine cyanide and reaction of the latter with pyridine to form glutaconic aldehyde which, in turn, interacts with barbituric acid and its derivatives to afford polymethine dyes, intensely coloured in the range 570–580 nm. This method makes it possible to detect thiocyanate ions up to 0.4 μg dm^{-3}.[3]

When concentration of thiocyanate is much higher than the above one, it can be detected by the addition of copper sulfate and *N*-ethyl-*N*-(2-hydroxyethyl)-1,4-phenylenediammonium sulfate with further extraction of a coloured compound formed. The range of determined concentrations of thiocyanate in the solutions with maximal optical density 528 nm is 15–45 mg dm^{-3}.[4] The coloured reaction of thiocyanate with $FeCl_3$ is used in the analysis of fossil water of oil fields. Fe^{3+} ions in the acidic medium ($pH \leqslant 0.2$) form complex compounds with thiocyanate coloured red.[5] The analysis of fossil water is complicated by high concentrations of the salts and oil colouring. Kinetic methods for determining thiocyanate ion are based on the oxidation rate in the presence of methyl orange, methyl red, methylene blue or crystal purple dyes.[6–8] The measurement is carried out by detection of the changing optical density of the solutions in the maximum of absorption corresponding to each dye.

We have proposed a transparent polymethacrylate matrix (PMM) with the immobilized complex of mercury and diphenylcarbazone (DPC–Hg) to be used, which provided both their sustainable ability to undergo analytical reaction and the optical effect of preserving media transparency.[9] The operation is based on colour change after the analyte is bound, which allows us to obtain visually observable and easily measureable analytical response.[10–14]

The combination of a coloured reagent and a transparent polymeric matrix demonstrates such advantages as concentrating, increased selectivity and sensitivity as compared to spectrophotometric techniques. Furthermore, the use of solid supports often provides environmental safety of the analysis due to a lower volume of toxic reagents and the possibility of their incorporation into the solid phase. Here we present the results of our study of the interaction between thiocyanate and the DPC–Hg complex immobilized in PMM to create a colorimetric sensor. PMM is a special material[15] bearing functional groups and possessing the ability to extract both the reagent and test substance. Transparent 10×10 cm polymethacrylate plates, thickness 0.60 ± 0.04 mm, were prepared by the radical block polymerization of methacrylate, polyethylene glycol PEG400 and alkaline earth metals at 60 °C for 3 h. Then these plates with immobilized DPC–Hg[†] were cut as 6.0×8.0×1.0 mm working platelets (weight *ca.* 0.05 g) for analyses. We used an initial PMM as a reference standard in the measurements of optical qualities of PMM with an immobilized reagent after contact with the analyte solution. In the presence of thiocyanate, depending on its concentration, the colour of the sensor changes from purple to pink because of destruction of the DPC–Hg complex (Figure 1). The pink colour of DPC in PMM remains when the complex with Hg^{II} is fully destroyed.

The effect of pH in the diphenylcarbazone solution on its immobilization into PMM and formation of the DPC–Hg complex was studied (Figure 2). As long as pH was raised, the absorption increased, became almost constant and reached its maximum at pH 4-6. The acetate buffer with pH 5.2 was chosen as an optimal one for immobilization of DPC–Hg and its interaction with the

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[†] Immobilization of DPC–Hg into PMM was performed by the sorption from the solution in a static mode in two steps. PMM was kept in alcohol solution of diphenylcarbazone (0.02 M) for 2 min, the matrix turned pink with absorption peak at 510 nm. Then the solution of Hg^{II} (0.05 M) was added and the sample was incubated for 8 min to result in a sensing element for determining thiocyanate, coloured dark-purple with absorption peak at 550 nm.

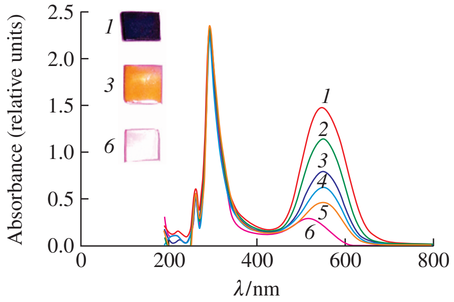

Figure 1 Absorption spectra and scanned images of the DPC–Hg in PMM samples after contact with the thiocyanate solution of various concentrations: (*1*) 0, (*2*) 1.0, (*3*) 2.0, (*4*) 4.0, (*5*) 10.0, and (*6*) 20.0 mg dm^{-3} (V = 50 ml, pH 5.2).

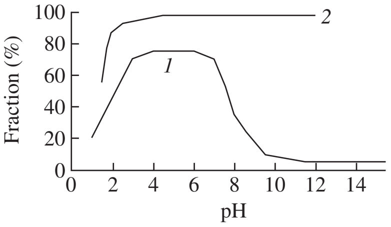

Figure 2 pH-Dependences of (*1*) the extraction of diphenylcarbazone and (*2*) the formation of DPC–Hg in PMM.

thiocyanate solution, since according to reported data,[16] at this pH, ions of many metals do not practically form complexes with immobilized DPC–Hg.

The incorporation of DPC–Hg into PMM influences both the optical density after the contact with the thiocyanate solution and the range of linearity of the analytical signal dependence on the concentration of the analyte in the test solution (Table 1). The amount of diphenylcarbazone in PMM varied with changing the time of the matrix contact with the reagent solution (Figure 3).[17]

Raising the reagent content in the matrix led to increase in both the linear dependence and the sensitivity coefficient of thiocyanate determination. The lowest limit of detection was observed for the matrixes with reagent content of 1.5 μmol g^{-1}, which were used in all further experiments.

The selectivity was measured under thiocyanate concentration 1.0 mg dm^{-3}, pH 5.2 and variable concentration of the concomitant substances. Thiocyanate determination was not prevented by the hundredfold amount of Fe$^{\mathrm{III}}$, Cu$^{\mathrm{II}}$, Hg$^{\mathrm{II}}$, Cr$^{\mathrm{III}}$, Co$^{\mathrm{III}}$, Pb$^{\mathrm{II}}$, Ni$^{\mathrm{II}}$ and Mn$^{\mathrm{II}}$, and tenfold amount of phosphates, sulfates and chlorides. The approbation was carried out on fossil and drill water samples to determine thiocyanate content in accordance with the calibration curve plotted under the corresponding conditions. The results of thiocyanate determination as tracer agent in oil-field brine and formation water samples are given in Table 2. The accuracy of the results was monitored by the analysis of spiked samples and comparison with the results of thiocyanate determination by FeCl$_3$ assisted spectrophotometric method. The results obtained indicate the satisfactory accuracy and reproducibility of the proposed technique for determination of thiocyanate.[18]

Table 1 Analytical characteristics of the solid phase spectrophotometric determination of thiocyanate using PMM.[a]

DPC-Hg in PMM matrix / μmol g^{-1}	Analytical range/ mg dm^{-3}	Detection limit/ mg dm^{-3}
0.8	1.4–5.0	1.0
1.5	0.8–50.0	0.5
2.1	0.8–80.0	0.6
2.6	1.8–100.0	1.1

[a] Time of contact of the matrix with the thiocyanate solutions is 15 min.

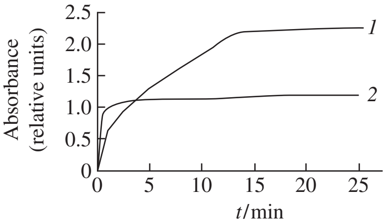

Figure 3 (*1*) Absorbance of diphenylcarbazone and (*2*) formation of DPC–Hg in PMM *vs*. contact time.

Table 2 Determination of thiocyanate in the samples (n = 5, P = 0.95).

Sample	Initial concentration / mg dm^{-3}	Determined concentration / mg dm^{-3}	S_r (%)	
Oil-field brine	0.0	0.99 ± 0.09 0.96 ± 0.07[a]	4.5 3.1	
Formation water	1.0	0.9 ± 0.2 1.0 ± 0.2[a]	7.1 7.2	+ VIS determination

[a] By spectrophotometric technique using Fe^{3+}.

Thus, the method of solid phase extraction and spectrophotometric determination of thiocyanate using PMM modified by DPC–Hg has been proposed. The developed procedure is simple and rapid, characterized by a low detection limit, and gives reliable results for all concentrations of thiocyanate in solutions in the covered range of 0.8–50 mg dm^{-3}.

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