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## Determination of the Adsorbed Quantities of Surfactants by IR-Spectroscopy

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Direct determination of the adsorbed amounts of surfactants on AgI by IR-spectroscopy is described. The adsorbed quantities are determined from the relationship between the intensities of the characteristic bands in IR-spectra of standard samples and the samples with adsorbed surfactants. The samples for IR-measurements are in the form of patterns consisting of AgI separated from the systems. The quantities of adsorbed sodium n-dodecyl sulphate, laurylamine nitrate and triton-X-305 are determined.

### INTRODUCTION

The adsorption of inorganic and organic species from solutions onto solids has been studied by various experimental techniques. Determination of the adsorbed quantities along with other parameters enables a better knowledge of the adsorption processes. The data could be obtained indirectly by material balance in the solution before and after the adsorption, or by measuring the relative change of some physical or chemical property which is caused by the adsorption process. These indirect methods are based on two suppositions: (i) material deficiency in the solution is caused by the adsorption process only, and (ii) there is a direct correlation between the adsorbed amount and some physical or chemical property of the system.

Direct determination of the adsorbed amounts is often impossible because the adsorbed quantities are too small. One of the few known methods which have been developed is based on radioactive tracers<sup>1</sup>. The adsorbed amount determined by this method is defined as the material carried by the adsorbent at the end of the experiment, i. e. after the adsorbent has been separated, washed and dried.

IR-spectroscopy has been employed along with other technique to study the adsorption processes and to determine the adsorbed amounts. Many techniques based on IR-spectroscopy have also been employed to study some physical or chemical properties of the species adsorbed on the surface<sup>2</sup>.

In this paper a simple method allowing a direct determination on of the adsorbed quantities of the surfactants by IR-spectroscopy is described. The

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method is applicable to the surfactants with convenient IR-spectrum which does not coincide with the spectrum of the adsorbent.

#### EXPERIMENTAL

The systems were prepared in the same way as in the experiments in which the radioactive tracer techniques were used<sup>1</sup>. The adsorbed amount was again defined as the quantity of the surfactant carried by AgI after its separation from the system.

The »fresh« systems were prepared by mixing the precipitational components (NaI and AgNO<sub>3</sub>) and surfactant. The component in excess (NaI or AgNO<sub>3</sub> for the preparation of negatively or positively charged AgI respectively) and surfactant were stirred by the magnetic stirrer and the second component was added continuously from the pipette. The systems were left to stand for 24 hours at 296 K. After that, solid AgI was separated from the solution by decantation, filtration through a filter paper and finally it was washed three times with the solution of the same pI or pAg as the mother liquor. The precipitates were dried at 333 K before the pellets for IR-measurements were prepared. The systems with »dried« precipitates were prepared by addition of isoelectrically performed, dried and crushed AgI to the solution containing the surfactant and NaI or AgNO<sub>3</sub>. The solid phase was separated from the solution one hour after the preparation of the system. Separation, washing and drying were done as described for the »fresh« systems. The samples for IR-measurements were in the form of pellets consisting of 200.0 mg dried AgI precipitate separated from the systems. The pressure of 150–200 kp cm<sup>-2</sup> was employed to form the pellets. IR-spectra were measured on the Perkin-Elmer Mod. 137 spectrophotometer.

The adsorbed quantities of the surfactants were determined from the relationship between the intensities of the characteristic bands in IR-spectrum of the standard sample and the sample with the adsorbed surfactant. The intensity was expressed in relative units as distance between the top of the band and the basic line of the spectrum. The adsorbed quantity in absolute units was calculated from the calibration curve, showing the relative intensity against the quantity of the surfactant in the standard sample. IR-spectra of the standard samples were obtained on several sets of homogeneous mixtures containing known quantities of crushed and dried isoelectric AgI and solutions of sodium n-dodecyl sulphate. The pellets for the calibration measurements were prepared with 200.0 mg of dried mixture.

#### RESULTS AND DISCUSSION

The investigations were carried out on AgI as adsorbent and sodium n-dodecyl sulphate as surfactant. Some results are also presented for several other surfactants.

AgI is the classical, most investigated colloidal model which has been used for studying the adsorption phenomena. The stability of AgI in the presence of sodium alkyl sulphate has also been investigated<sup>3</sup>. AgI and sodium alkyl sulphates have IR-spectra convenient for the investigation of adsorption. Isoelectrically precipitated AgI has no bands in the IR-spectrum in the range of 700 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>, while the spectrum of sodium n-dodecyl sulphate<sup>4</sup> shows marked bands of CH- and SO-vibration band at 2924 cm<sup>-1</sup> and 1227 cm<sup>-1</sup> respectively. The investigation of adsorption of sodium n-dodecyl sulphate was carried out at a concentration of 0.01 mol dm<sup>-3</sup> AgI at pAg = 3 and pI = 3. The concentration of the surfactant was in the region of AgI flocculation.

Figure 1 shows the IR-spectra of standard samples. The calibration curves drawn in Figure 2 were determined at 2924 cm<sup>-1</sup> and 1227 cm<sup>-1</sup>.

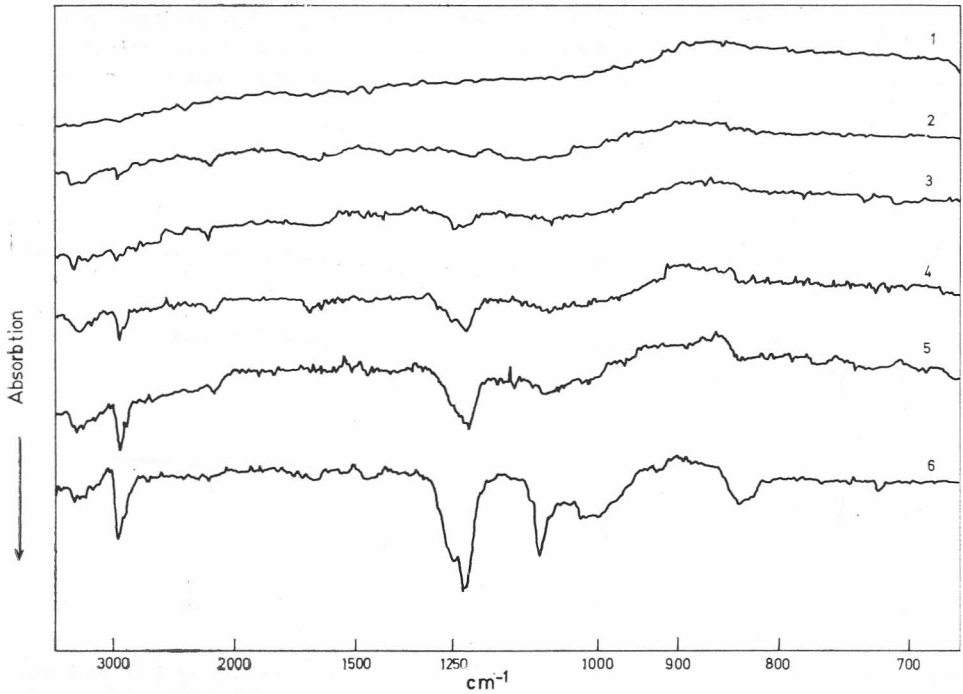


Figure 1. IR-spectra of standard samples containing: (1) pure AgI; (2) 0.05; (3) 0.125; (4) 0.25; (5) 0.50; (6) 1.25 millimole of sodium n-dodecyl sulphate per mole AgI.

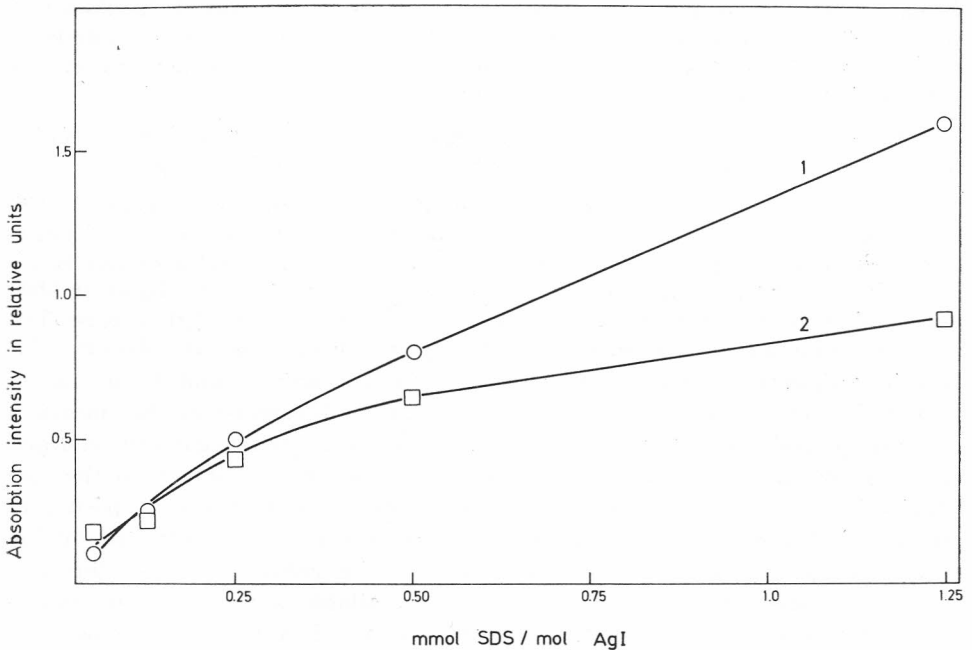


Figure 2. Calibration curves determined at: (1) 2924 cm<sup>-1</sup>; (2) 1227 cm<sup>-1</sup>.

Figure 3 shows the IR-spectra of positively charged AgI systems at three concentrations of sodium n-dodecyl sulphate. An increased concentration of the surfactant causes a marked increase of CH-vibration band intensity at  $2924\text{ cm}^{-1}$ .

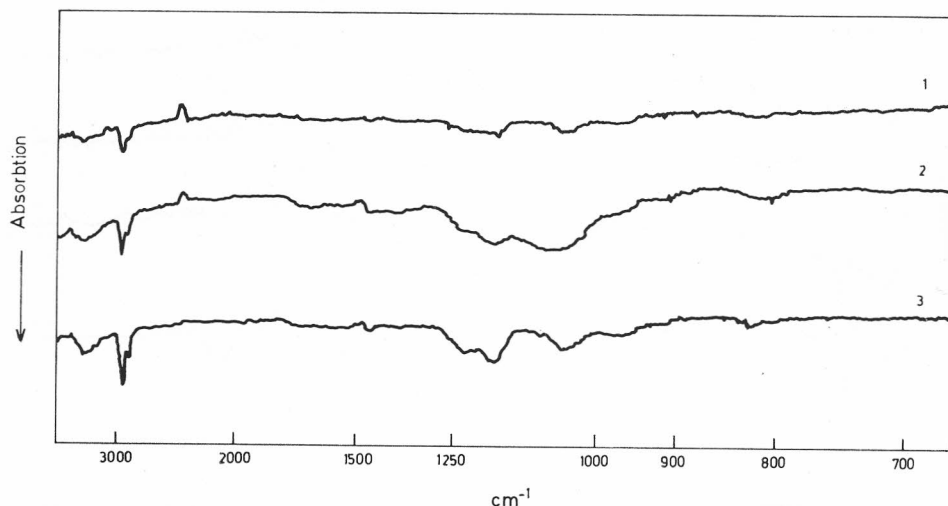


Figure 3. IR-spectra of AgI separated from the systems containing  $0.01\text{ mol dm}^{-3}$  AgI at  $\text{pAg} = 3$  and the concentrations of sodium n-dodecyl sulphate: (1)  $6.0 \times 10^{-5}$ ; (2)  $1.0 \times 10^{-4}$ ; (3)  $1.6 \times 10^{-4}$ .

From IR-spectra in Figure 3 and the calibration curve no. 1 in Figure 2 the adsorbed amounts of 0.20, 0.30 and 0.70 millimole of sodium n-dodecyl sulphate per mole AgI were determined for the surfactant concentrations of  $6.0 \times 10^{-5}$ ,  $1.0 \times 10^{-4}$  and  $1.6 \times 10^{-4}\text{ mol dm}^{-3}$  respectively.

Figure 4 shows the IR-spectra of negatively charged AgI systems containing  $6.0 \times 10^{-5}$  and  $1.6 \times 10^{-4}\text{ mol dm}^{-3}$  of sodium n-dodecyl sulphate.

In this case, some irregularity in the IR-spectra and a new band at  $1600\text{ cm}^{-1}$  could be seen. The  $1600\text{ cm}^{-1}$  band appears only in the spectra of negatively charged AgI precipitate. It does not appear in the spectra of isoelectric or positively charged AgI. Hence, it can be concluded that the band at  $1600\text{ cm}^{-1}$  is due to the interaction of iodide ions adsorbed on the AgI surface. The adsorbed amounts of sodium n-dodecyl sulphate determined at  $2900\text{ cm}^{-1}$  for two investigated concentrations of the surfactant were found to be below 0.05 millimole per mole AgI. A relatively large difference in the adsorbed amounts of sodium n-dodecyl sulphate on positively and negatively charged AgI systems might be due to a different effect of the surfactant on the stability of these systems<sup>3</sup>. The adsorption of anionic surfactants on positively charged AgI systems takes place at the sites on the surface occupied by the potential-determining silver ions and also, as the concentration of the surfactant increases, at some other sites<sup>5</sup>. The available number of sites determines the adsorbed amount. On negatively charged AgI systems some sites are occupied by iodide ions and the anionic surfactants can adsorb only at

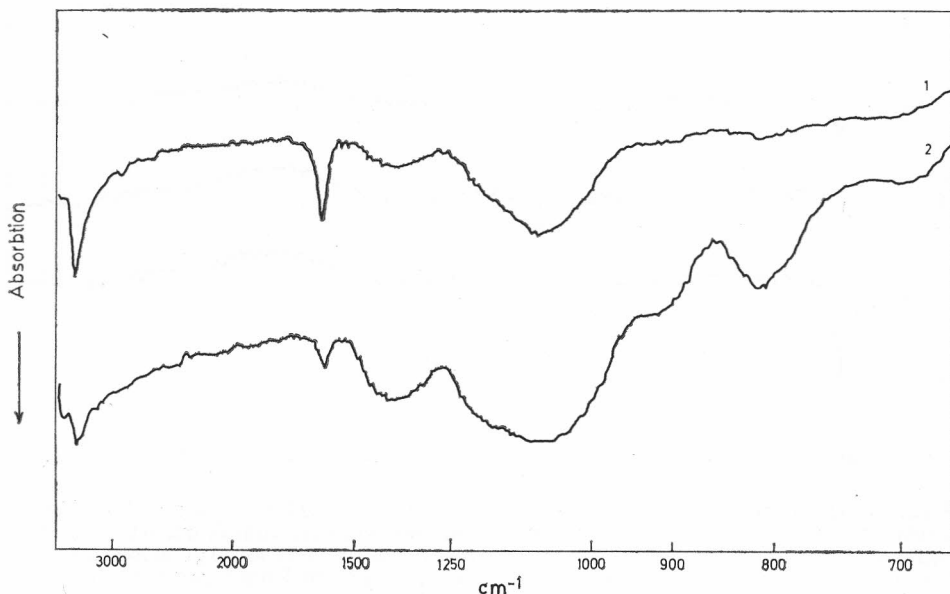


Figure 4. IR-spectra of AgI separated from the systems containing  $0.01 \text{ mol dm}^{-3}$  AgI at  $pI = 3$  and the concentrations of sodium n-dodecyl sulphate: (1)  $6.0 \times 10^{-5}$ ; (2)  $1.6 \times 10^{-4} \text{ mol dm}^{-3}$ .

the other sites. Consequently, a smaller number of available sites should cause a lower adsorption of the surfactant as it is clearly demonstrated for the negatively charged AgI systems. The adsorption of sodium n-dodecyl sulphate on the positively charged AgI results in the coagulation process, while on the negatively charged AgI a process similar to the coagulation process occurs<sup>3</sup>. The effect of laurylamine nitrate<sup>6</sup> and triton-x-305<sup>7</sup> on ion adsorption was studied earlier. Therefore, it was interesting to determine the amounts of these surfactants adsorbed on AgI. The IR-spectroscopy could be applied, since IR-spectra of these substances have marked bands<sup>4</sup>. Figure 5 shows the IR-spectrum of the standard sample of 0.25 millimole laurylamine nitrate per mole of isoelectric AgI together with the spectra of AgI separated from the systems with  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$  laurylamine nitrate at  $pI = 5$  and  $pAg = 5$ .

Figure 5 shows a prominent feature of CH-vibration band. From the intensity of this band it was calculated that the amount of adsorbed laurylamine nitrate was about 0.58 millimole per mole of negatively charged AgI, and about 0.3 millimole per mole of positively charged AgI. It can be concluded that the positively charged laurylamine ion is adsorbed on the positively charged AgI, but the adsorbed amount is lower than the adsorbed amount of the same species on the negatively charged AgI.

It was shown previously<sup>7</sup> that the non-ionic triton-x-305 molecule has a significant influence on the ion adsorption and on the dispersity of AgI

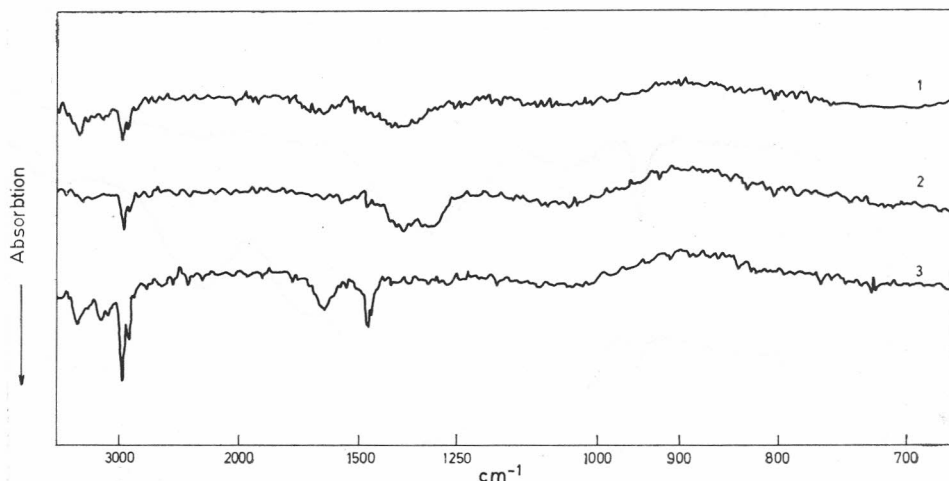


Figure 5. IR-spectra of: (1) standard sample containing 0.25 millimole of laurylamine nitrate per mole AgI; (2) AgI separated from the systems containing  $0.01 \text{ mol dm}^{-3}$  AgI and  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$  laurylamine nitrate at  $\text{pI} = 3$ ; (3) AgI separated from the systems containing  $0.01 \text{ mol dm}^{-3}$  AgI and  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$  laurylamine nitrate at  $\text{pAg} = 3$ .

systems. The presence of triton-x-305, the structure is given in Figure 6, in a wide range of concentrations causes the high stability of »fresh« AgI systems, which makes the separation of AgI for IR-spectroscopy investigations rather difficult.

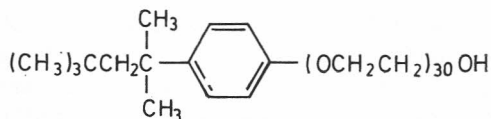


Figure 6. Triton-x-305.

For this reason the adsorption of triton-x-305 was investigated on »dried« AgI systems.

Figure 7 shows the IR-spectrum of the standard sample containing 0.25 millimole of triton-x-305 per mole of isoelectric AgI together with the spectra of AgI separated from the systems with triton-x-305 in the concentration of  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$  at  $\text{pI} = 3$ ,  $\text{pAg} = 3$  and without NaI or AgNO<sub>3</sub>. From the intensities of the marked bands in the spectra, the adsorbed amounts of about 0.09 millimole triton-x-305 per mole AgI in all three systems were calculated. The obtained results indicate the ability of triton-x-305 to adsorb on AgI of different charges.

From the obtained results, it is obvious that the adsorbed quantities of surfactants could be determined by measurements of CH-vibration band intensities. The determination of the adsorbed amounts by measurements of CH-vibration bands was reported previously in the literature<sup>8</sup>, where the adsorbed quantities were determined from the concentration difference in the solution.

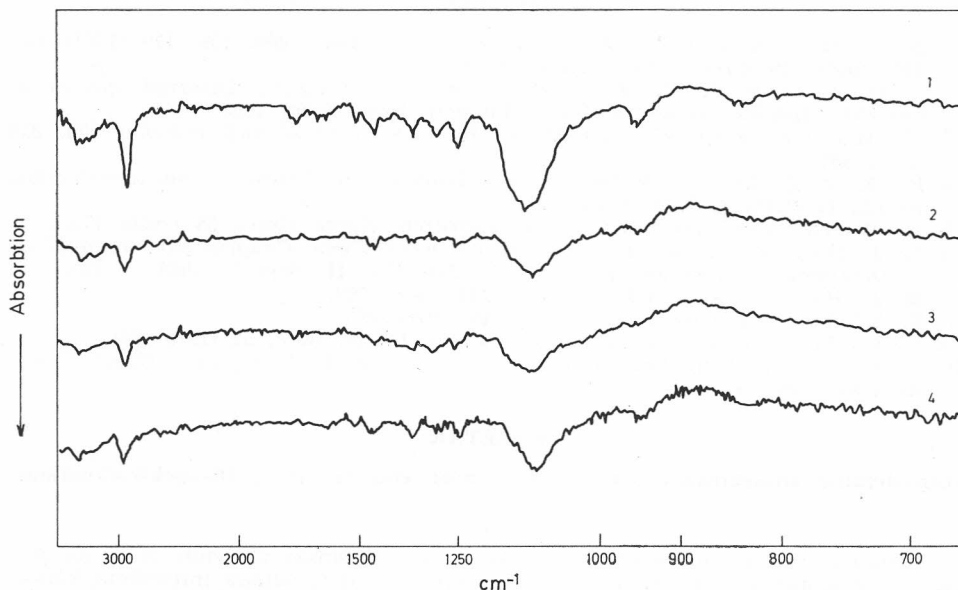


Figure 7. IR-spectra of: (1) standard sample containing 0.25 millimole triton-x-305 per mole AgI; (2) AgI separated from the systems containing  $0.01 \text{ mol dm}^{-3}$  isoelectrically precipitated and dried AgI and  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$  triton-x-305. There is no added NaI or  $\text{AgNO}_3$ ; (3) AgI separated from the systems containing  $0.01 \text{ mol dm}^{-3}$  isoelectrically precipitated and dried AgI and  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$  triton-x-305 at  $\text{pAg} = 3$ ; (4) AgI separated from the systems containing  $0.01 \text{ mol dm}^{-3}$  isoelectrically precipitated and dried AgI and  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$  triton-x-305 at  $\text{pI} = 3$ .

In addition, measurements of heights of the characteristic peaks of IR-spectra served for the direct determination of sorption capacities of several adsorbents<sup>9</sup>. The irregularities in bands of the active parts of surfactants observed in IR-spectra prevent a direct determination of the adsorbed quantities, although these phenomena accompanied with some theoretical statements could serve for a study of the adsorption on the surfaces<sup>10</sup>.

#### CONCLUSION

The results clearly show that the IR-spectroscopy technique is applicable in direct determinations of the adsorbed quantities of surfactants. It was found that sodium n-dodecyl sulphate and laurylamine nitrate are adsorbed on both, the negatively and positively charged AgI. However, the adsorption amount on the AgI charged by the same charge as the surfactant ion, is smaller than the adsorption amount on the oppositely charged AgI.

Different adsorption of sodium n-dodecyl sulphate on positively and negatively charged AgI can be directly correlated with the different effect of this surfactants on the stability of the oppositely charged AgI.

The results of the study of triton-x-305 adsorption show that this non-ionic molecule undergoes adsorption on AgI. The adsorbed amounts were found to be independent of the AgI charge.

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## SAŽETAK

**Određivanje adsorbiranih količina površinski aktivnih tvari IR-spektroskopijom***M. Hus*

Opisano je izravno određivanje adsorpcije površinski aktivnih tvari na AgI IR-spektroskopijom. Adsorbirane količine određene su iz odnosa intenziteta karakterističnih vrpca IR-spektra standardnog uzorka i uzorka s adsorbiranom površinski aktivnom tvari. Uzorci za IR-mjerenja u obliku su pastila AgI odijeljenog iz sistema. Određene su adsorbirane količine natrij-n-dodecil sulfata, laurilamin-nitrata i triton-X-305.