

was optimized with respect to sample preparation and the ratio between the solvent and the sample.

**Analytical procedure.** The soil sample (50 g) is mixed with  $H_3PO_4$  (85%, 1 ml) and  $Na_2SO_4$  (20 g, p. a.). The solid mixture is placed in prewashed extraction thimbles and extracted in a Soxhlet apparatus with toluene (100 ml, nanograd). The solution may be concentrated by a factor of about 2. After the extraction, the amount of toluene is determined. 10 ml of the extract are combusted in a  $H_2/O_2$  flame (Wickbold apparatus) following the general procedure described for EOX of effluent water [3]. HCl is absorbed in NaOH (0.1 N, 25 ml); after combustion, the apparatus is rinsed with NaOH until a volume of 100 ml is yielded in the absorption chamber. The chloride is determined by potentiometric titration (detection limit 0.2 ppm), by turbidimetric analysis (detection limit 1 ppm) or by Mohr titration (detection limit about 50 ppm). In practice, the limit of quantitation is about 5 ppm for potentiometric titration and turbidimetric analysis of chloride. The chemicals as well as the glassware used have to be checked thoroughly for traces of chloride.

In Table 1, the results of 4 round robin samples are presented. Each sample was extracted four times, each extract was analyzed at least twice mostly leading to nearly identical results.

As may be taken from Table 1, the samples were very heterogeneous yielding relatively high standard deviations. The interlaboratory standard deviations and the standard deviations within each laboratory are of the same magnitude thus indicating the successful adaption of the method.

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## Determination of cationic surfactants in clay minerals\*

H. Klotz

Hoechst AG, Analytisches Labor G 865, Postfach 8003 20, D-6230 Frankfurt 80, Federal Republic of Germany

### Bestimmung von kationischen Tensiden in Tonmineralien

#### 1. Introduction

Cationic surfactants, especially of the distearyl-dimethyl-ammonium-chloride type, are widely used in the Federal Republic of Germany, particularly as fabric softeners. Their environmental behaviour is mainly determined by elimination through adsorption in activated and inactivated material and by the formation of electroneutral salts with the anionic surfactants that are usually present in excess.

The in some cases irreversible exchange and adsorption processes in clay minerals (especially phyllosilicates), or other inorganic substance such as are present in activated sludge are an important stage of elimination for the cationic surfactants. A montmorillonite, which is charged with technical distearyl-dimethyl-ammonium ions and is a phyllosilicate which binds cationic surfactants particularly firmly by ion exchange, was selected as the model substance for the determination of cationic surfactants in clay minerals.

#### 2. Results

**2.1 Model substance.** Organophilic bentonite "Bentone 34" Kronos Titan GmbH (montmorillonite charged with about 34% distearyl-dimethyl-ammonium ions instead of sodium) containing nitrogen: 0.875%  $\cong$  33.7 distearyl-dimethyl-ammonium ions (molar mass: 540.5 g/mol).

\* Dedicated to Prof. Dr. Harnisch on the occasion of his 60th birthday

**2.2 Determination of the distearyl-dimethyl-ammonium ions by extraction.** Only small amounts of cationic surfactants (< 10%) can be extracted with simple organic extractants such as chloroform and methanol. Organic extractants, admixed with salts or concentrated hydrochloric acid [1, 2], extract up to 30% cationic surfactant. Extraction with methanolic hydrochloric acid yields recoveries of between 60 and 70%. These extractants which destroy the inorganic matrix only partially or not at all, do not yield a satisfactory recovery (Table 1).

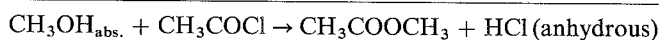
**2.3 Determination of the distearyl-dimethyl-ammonium ions after destruction of the silicate matrix with hydrofluoric acid.** Cationic surfactants can be determined with recoveries in the region of 95%, when the silicate matrix is destroyed by evaporating with 40% hydro-fluoric acid and extracting the evaporating residue with chloroform (Table 2).

#### 3. Experimental

**3.1 Analytical methods for the final determination of cationic surfactants.** Two-phase titration according to DIN, ISO 2871; disulphine blue method [3, 4].

**Table 1.** Recoveries for various extractants. Distearyl-dimethyl-ammonium ions as a percentage of the theoretical yield (34% is equated to 100%)

$H_2O$	0%
$CHCl_3$	2%
$CH_3OH$	4%
$CH_3OH/NH_4OAc$ (2/1 – v/m)	18%
$CH_3OH/HCl$ (25/1 – v/v)	24%
$CH_3OH/C_2H_5OH/CHCl_3/HCl_{conc.}$ (1/1/1/1)	28%
meth. HCl (2 mol/l)	61%
meth. HCl (4 mol/l)	72%



**Table 2.** Recoveries for various decomposition methods

Method of decomposition	Recovery Distearyl-dimethyl-ammonium ions (%)		Recovery Distearyl-dimethyl-ammonium ions in Bentone 34 (%) (34% = 100%)	
	Two-phase titration	DSB method	Two-phase titration	DSB method
Evaporated in an open platinum dish with 40% hydrofluoric acid	— 91 96 93	90 — 88 —	— 97 85 102	79 — — —
Decomposed for 3 h with 48% hydrofluoric acid in a bomb at 130°C and then evaporated in an open platinum dish	89	—	91	—
Decomposed for 3 h with 40% hydrofluoric acid in a bomb at 100°C and then evaporated in an open platinum dish	86	83	111	—

DSB Disulphine blue

### Spectrophotometric microanalysis of silicate rocks for manganese after fusion with a lithium carbonate — boric acid mixture

Rokuro Kuroda, Yoshihiko Matsuzawa, and Koichi Oguma

Laboratory for Analytical Chemistry, Faculty of Engineering, University of Chiba, Chiba, Japan

### Spektrophotometrische Mikroanalyse von Silicatgesteinen für Mangan nach Aufschluß mit Lithiumcarbonat/Borsäure

Manganese in silicate rocks has been determined most commonly by permanganate method, but it lacks sensitivity in microchemical analysis. An alternative method for determining manganese is that based on the reaction of manganese with formaldoxime in alkaline media [1]. The sensitivity of the determination is claimed to be approximately five times that based on the permanganate formation. The most serious interference comes from iron which forms a highly coloured complex with formaldoxime.

In this communication polyvalent cations including iron, aluminium, titanium have been removed simply by cation-exchange with P-cellulose, so that interferences of coloured

3.2 *Procedure for extraction.* 500 mg "Bentone 34" are introduced into a 50 ml roundbottomed flask and stirred under reflux for 1 h with 10 ml extractant. The suspension is then cooled and transferred in to a 10 ml polypropylene centrifuge tube with a disposable syringe. The flask is rinsed with extractant, the centrifuge tube filled up to the top and then sealed by melting. After centrifuging, an aliquot of the clear, supernatant phase is removed and the distearyl-dimethyl-ammonium ions content determined by mixed indicator two-phase titration.

3.3 *Procedure for hydrofluoric acid decomposition.* 400 mg "Bentone 34" are admixed with 3 ml of 40% hydrofluoric acid in a platinum dish. The hydrofluoric acid is evaporated (about 2 h). The residue is three times extracted by boiling with methanol/CHCl<sub>3</sub>, each time. The methanol solution is concentrated on a rotary evaporator, evaporated in a dish and weighed. The evaporation residue is transferred in to a 25 ml graduated flask with chloroform and filled up. A 10 ml aliquot of this is removed for mixed indicator two-phase titration and 50 µl is taken for spectrophotometric determination with disulphine blue.

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complexes of iron as well as troublesome hydrolytic precipitation of polyvalent cations in alkaline media are eliminated to permit the direct application of the formaldoxime method. The results for the determination of manganese in a variety of standard silicate rocks will be demonstrated.

### Experimental

#### Reagents and apparatus

*Formaldoxime solution* (0.2 M). Dissolve 5 g of hydroxylamine hydrochloride in water, add 2.5 ml of 36% formaldehyde solution and dilute to 50 ml with water.

*Standard manganese solution.* 1.004 mg Mn/ml of 1 M HCl for atomic absorption spectrometry use.

*Buffer solution.* Dissolve 35 g of ammonium chloride in 200 ml of water and add 300 ml of ammonia solution (pH 10.8).

*Sodium potassium tartrate solution.* Dissolve 15 g of the tartrate in water to give 15% (w/v) solution.

*P-cellulose.* Whatman P 11 cellulose phosphate, fibrous cation exchanger for chromatographic use.

Unless otherwise mentioned, analytical reagent grade chemicals were used throughout.

A Hitachi 220 A type double beam spectrophotometer with 20 mm glass cells was used for the photometric measurements.

Offprint requests to: R. Kuroda