

# Determination of superabsorbent polyacrylate dust in workplace atmospheres after derivatization with ethanol and using HPLC with pulsed electrochemical detection

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Received 10th March 2000, Accepted 15th August 2000

First published as an Advance Article on the web 18th September 2000

Superabsorbent polyacrylates (SAPs) have been used in the hygiene industry for many years. A derivatization and analytical method was developed for routine analysis of trace levels of SAP dust in workplace atmospheres. In comparison with existing methods, which are based on the sodium content or the ion exchange properties of the polymer, this method is more specific. It has the advantage of not being influenced by any sodium containing contaminants. Air samples are collected on Teflon filters using air monitoring sampling cassettes. The filters are subsequently placed in quartz vials and a reaction mixture containing hydrochloric acid in ethanol is added. The hydrochloric acid–ethanol solution, when heated, converts the carboxylic acid groups on the backbone of the insoluble polyacrylate into ethyl esters. After reaction, the excess of ethanol and hydrochloric acid is completely removed under vacuum. The sample is then treated with aqueous sodium hydroxide at 80 °C to release the bound ethanol. The solution is analyzed by HPLC on an anion exclusion stationary phase using dilute perchloric acid as mobile phase. Ethanol is identified and quantified with a pulsed electrochemical detector. Several environmental samples in addition to laboratory spiked samples were successfully analyzed with this technique. Recoveries averaged >85% for spiked blank filters at levels from 5 to 50 µg per filter with relative standard deviations up to 7%. The instrument's limit of detection (LOD) for ethanol was 0.1 mg l<sup>-1</sup>. The LOD for derivatization and analysis corresponds to 3 µg of SAP per filter (assuming an esterification factor of 0.30 µg of ethanol per µg of SAP).

## Introduction

Superabsorbent polyacrylates are formed by the production of long, repeating chains of acrylic acid. Most of them are cross-linked sodium polyacrylates. Referred to as 'absorbent gelling materials', 'superabsorbent polymers' (SAPs) or 'polyacrylate absorbents', they are used in a variety of industrial and consumer products.<sup>1</sup> Their structure gives them the unique ability to absorb and retain large quantities of water or aqueous solutions. Therefore, SAPs have improved personal care products such as baby diapers, adult incontinence products and feminine hygiene products.

Safe work practices are one of the most important factors in the control of dust exposure when handling SAPs. The commercial SAPs consist of particles averaging 300–800 µm. However, during production, handling and shipping, very small amounts of respirable particles (diameter <10 µm) may be generated which have the potential for inhalation. In the 'List of MAK and BAT Values 1999' published by the German DFG,<sup>2</sup> polyacrylic acid (neutralized, cross-linked) has been listed with a MAK value of 50 µg m<sup>-3</sup> for the respirable fraction which reaches the alveoli.

Because of the insolubility of SAP dust, analyses in the microgram range are much more difficult than for other organic airborne pollutants. To conduct the routine monitoring of workplace levels of SAP, an accurate, safe and relatively simple analytical method is needed.

The IPA and EDANA have published methods based on the extraction of sodium from the polymer with subsequent analysis by atomic absorption or atomic emission spectroscopy.<sup>1,3</sup> Knowing the sodium content in the handled bulk material, the

measured amount of sodium on the filter could be correlated with the SAP content in the sampled air. Because of the ubiquity of sodium in the environment, great caution against sodium contamination of the sampling and analysis steps is needed.

The US National Institute for Occupational Safety and Health (NIOSH) has published a method<sup>4</sup> using copper sulfate solution to add copper to the polymer dust to exchange sodium, followed by atomic absorption spectroscopy. However, it has been reported that this method has not demonstrated sufficient sensitivity for the concentration range of interest in the workplace.<sup>1</sup> Another method that has been developed uses an extraction solution containing europium.<sup>5</sup> The europium is retained by the polymer and can be measured by neutron activation analysis, for instance. Initial attempts have also been described to quantify polyacrylate polymers by the formation of propyl esters with subsequent gas chromatography (GC),<sup>6,7</sup> but neither direct GC of the reaction solution nor headspace GC provides the sensitivity necessary to determine polyacrylate dust at micrograms per cubic meter levels.

Furthermore, the so-called 'sodium method' and the other techniques mentioned have the great disadvantages that they respond to any environmental dust containing sodium, such as special types of fluff used in diaper production, or suffer interference from other contaminants.

The technique presented in this paper was designed to reduce these problems by modifying some aspects of the previously described esterification methods and using HPLC with pulsed electrochemical detection to improve the sensitivity. The method is applicable to the determination of free or partially neutralized forms of cross-linked polyacrylates and is independent of the cation of the salt.

## Experimental

### Materials

Air samples were collected on 37 mm Teflon filters (Millipore, Bedford, MA, USA; type Fluoropore, Article No. Fal 0 37 00) using the personal sampling equipment P.G.P. recommended by the German BIA (Berufsgenossenschaftliches Institut für Arbeitssicherheit), with a particle size separator (cyclone, SKC, Eighty Four, PA, USA). For the derivatization and saponification procedure, 10 ml quartz vials with screw-caps containing Teflon seals (made in-house) and a vacuum drying oven were used.

Two variable-volume pipetters (Eppendorf, Westbury, NY, USA) with ranges of 0.5–2.5 ml and 0.1–100  $\mu\text{l}$  were used for the addition of standards, spikes and other solutions. A ball mill (Fritsch, Idar-Oberstein, Germany; type Pulverisette) was used for micronizing the bulk SAP materials to an average particle size of approximately 10  $\mu\text{m}$ . The particle size distribution of the micronized material was measured by laser diffraction (Helos/Rodos-System from Sympatec, Clausthal-Zellerfeld, Germany).

An analytical balance (Sartorius, Westbury, NY, USA; type MC1, Research RC 210 D) with an accuracy of 0.01 mg was used for weighing aliquots of SAP spiking solutions and sieving fractions. A microbalance (Sartorius; type M5P) with an accuracy of 0.001 mg and a sieve shaker (Retsch, Haan, Germany; type KS 1000) with stainless steel sieves (45, 106, 150 and 300  $\mu\text{m}$ ) were used for testing the influence of particle size on derivatization yield.

### Chemicals

Ultrapure water purchased from Merck (Darmstadt, Germany) was used to prepare aqueous solutions and mobile phases. Ethanol (analytical-reagent grade) and butan-1-ol (analytical-reagent grade), perchloric acid (70%) and sodium hydroxide pellets were obtained from Riedel-de Haën (Seelze, Germany). Hydrochloric acid (36%; ultrapure reagent) was purchased from J. T. Baker (Gross Gerau, Germany). Commercially available superabsorbent polymers were used for the development of the described method. The accuracy and precision tests were carried out with the micronized product Sanwet IM 3900 (average particle size < 5  $\mu\text{m}$ ).

### Standards and solutions

A stock standard solution was prepared by dissolving 200.0 mg of ethanol in 100.0 ml of sodium hydroxide solution (0.2 mol  $\text{dm}^{-3}$ ). Aliquot volumes (100  $\mu\text{l}$  to 5 ml) were transferred into 1000 ml calibrated flasks and filled to the mark with 0.2 M sodium hydroxide solution to give standard solutions in the range 0.2–10 mg  $\text{l}^{-1}$  to construct a calibration curve. Spike solutions of SAP products were prepared by adding known amounts of micronized SAP material to 50 g of butan-1-ol in a glass bottle. Nominal concentrations were in the region of 1  $\mu\text{g}$  per milligram of butan-1-ol. The spike solutions were suspensions of small particle size polymer. Therefore, it was necessary to assure a homogeneous suspension by stirring even during the period when an aliquot was removed. The derivatization solution contained ethanol and hydrochloric acid (36%) in the proportions 1 + 1 (v/v). The mobile phase for the HPLC analyses was prepared by dissolving 8.5 ml of perchloric acid (70%) in 2000 ml of ultrapure water. The solution was stored under an oxygen atmosphere.

### Instrumental conditions

Ethanol was determined on a Dionex (Sunnyvale, CA, USA) Model 4000 ion chromatograph equipped with a gradient pump,

an eluent gas module, an autosampler and a PED-2 programmable electrochemical detector with a solid silver/silver chloride reference electrode and a platinum working electrode. The data acquisition software used to process the store results was first Dionex AI-450 integration software version 3.31 and later PeakNet 5.1 software.

The separation column used consisted of a Dionex ICE-AS 1 anion exclusion stationary phase connected to a Dionex Omnipack PCX 500 guard pre-column. The solvent used as mobile phase was a 50 mM aqueous solution of perchloric acid. The flow rate was 0.8  $\text{ml min}^{-1}$  under isocratic conditions and the injection volume was 100  $\mu\text{l}$ . The separation column was placed in a thermostat to maintain a constant temperature of 23 °C.

At the pulsed electrochemical detector (PED) the following potential–time (*E-t*) waveform was selected: start, 0.3; 0.28 s, 0.3; 0.29 s, 1.4; 0.34 s, 1.4; 0.35 s, –0.45; 0.89 s, –0.45; and 0.90 s, 0.3 V. The integration time for ethanol determination was between 0.21 and 0.25 s.

### Workplace samples

A variety of workplace samples were obtained from the Clariant in the SAP production plant (Site Cassella-Offenbach, Frankfurt, Germany) and from SAP converter plants. All these samples were used to test and validate the method. In one case two sets of samples were taken in parallel in order to compare this method with the sodium method.<sup>3</sup>

### Derivatization procedure

A Teflon filter from a workplace sample or a spiked filter or an exactly weighed amount of SAP material was transferred into a 10 ml quartz vial with a screw-cap. In the case of field samples, the inner surface of the sampling cassette was rinsed with 2 ml of ethanol directly into the reaction vial. Then, 4 ml of the derivatization solution were added so that the total volume covering the filter was at least 6 ml. The open vial was placed in a vacuum drying oven at 80 °C for 2 h without vacuum. Subsequently, the vacuum pump was switched on and the excess ethanol–hydrochloric acid mixture was removed at 80 °C. The sample was allowed to dry for at least 8 h at this temperature under reduced pressure (< 200 mbar).

### Saponification procedure

After the derivatization step, the dried sample was allowed to cool to room temperature, then 100  $\mu\text{l}$  of butan-1-ol were directly added to the filter as a ‘wetting agent’. The saponification solution was prepared by adding 0.9 ml of ultrapure water, followed by 20  $\mu\text{l}$  of sodium hydroxide solution (50%) which was always prepared from pellets directly before use. The vial was tightly capped and heated at 80 °C for 2 h. After cooling to room temperature the vial was opened and 1 ml of ultrapure water was added. The solution was then used directly for HPLC analysis.

### Esterification factor (EF)

The esterification factor represents the yield of esterification and hydrolysis. It depends on the specific superabsorbent polymer type and has to be determined individually for each bulk product.

The esterification factor is defined as

$$\text{EF} = \frac{\mu\text{g ethanol}}{\mu\text{g polyacrylate}} \quad (1)$$

The determination was performed by transferring a known amount of the SAP spike solution into the quartz vial and allowing the butan-1-ol to evaporate overnight. Appropriate amounts for validation experiments were in the range 30–60 µg. The aliquots removed from the spike solution were weighed in order to minimize the error. For each product type the esterification factor was determined at least 10 times. All ethanol values presented have been converted to the equivalent superabsorbent polymer value using the product specific esterification factor.

### Calculation

The concentration of ethanol in the sample solution after hydrolysis was calculated by the data system on the basis of the calibration curve.

The amount of SAP on the filter (mg) was calculated according to the equation

$$F = \frac{A \times V \times 100}{EF \times 1000 \times R} \quad (2)$$

where  $A$  is the concentration of ethanol in the hydrolyzed solution ( $\text{mg l}^{-1}$ ),  $V$  is the volume of the hydrolyzed solution (ml) and  $R$  is the recovery (%).

The SAP concentration in the air sample ( $\text{mg m}^{-3}$ ) was calculated according to the equation

$$W = \frac{F \times 1000}{L} \quad (3)$$

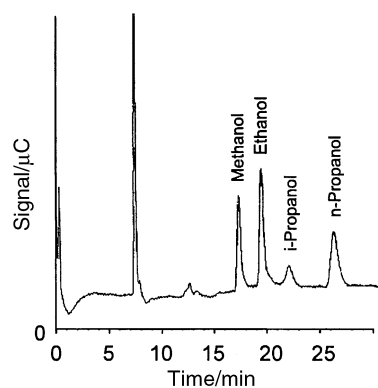
where  $L$  is the volume of air sample (l).

### Influence of particle size

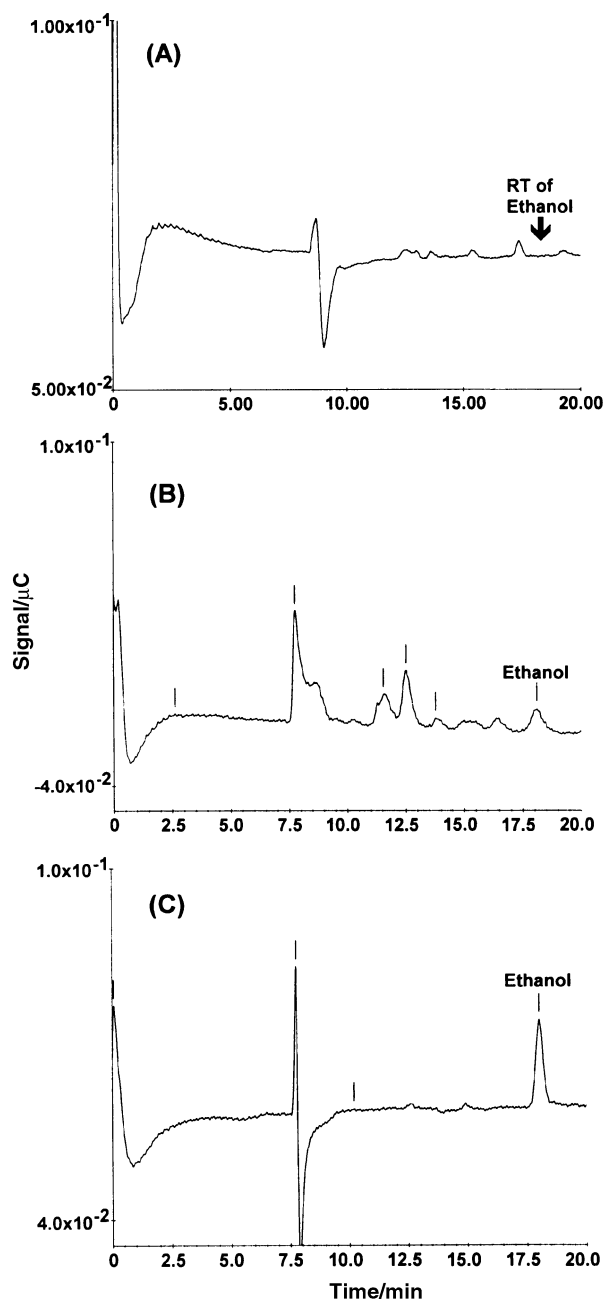
The esterification factors of different particle size fractions of superabsorbent polymers were determined. A set of screens in order from pan, 45, 106, 150 and 300 µm at the top was placed on a sieve shaker. A 50 g amount of the SAP material Sanwet IM 7100 was transferred to the top sieve, the sieve shaker was set to 90% intensity and the sample was then sifted for 10 min. From each fraction a maximum of 1 mg was weighed and transferred into a quartz vial. The derivatization and analyses were performed as described above. All tests were carried out in triplicate.

### Accuracy and precision study

Blank Teflon filters were placed in quartz vials and spiked with micronized SAP material at 5, 10, 20 and 50 µg levels. Samples



**Fig. 1** HPLC trace demonstrating the selectivity of the ICE-AS 1 column for separating aliphatic alcohols. Standard solution containing 2.5 mg of each alcohol in 1000 ml of 0.2 M sodium hydroxide.



**Fig. 2** Representative HPLC traces for (A) derivatization and saponification blank, (B) blank of Teflon filters and (C) standard solution of 1.0 mg of ethanol in 1 l of 0.2 M sodium hydroxide.

for each level were analyzed 10 times to calculate the standard deviation. The results found for SAP on the filters were compared with the amounts added to determine the recovery. Derivatization and HPLC analyses were performed as described above.

### Interference study

Different fluff types, bleached and non-bleached, were tested for their contribution to ethanol formation and their influence on the chromatographic separation. Approximately 0.5–1.0 mg of fluff was weighed into a quartz vial and derivatized and analyzed as described above. The following fluff types were investigated: Pulp Rayonier (bleached), Pulp Weyerhäuser (bleached), Pulp Tenung (non-bleached), Pulp Inco (non-bleached), Pulp Paper Supersoft and CTMP fluff.

## Results and discussion

### HPLC with electrochemical detection

Short-chain aliphatic alcohols can be determined by pulsed electrochemical detection at platinum electrodes in alkaline and acidic solutions.<sup>8</sup> A potential–time ( $E-t$ ) waveform as described above with a short current sampling period at 300 mV was found to be most suitable for ethanol with respect to high sensitivity and a sufficient signal-to-noise-ratio.

The ICE-AS 1 anion exclusion column turned out to be most convenient for the chromatographic separation of ethanol from matrix interferences. Using perchloric acid as mobile phase, maximum selectivity was achieved. Other short-chain alcohols were fully separated from ethanol (Fig. 1). The ethanol calibration curve was linear over the range 0.2–10 mg l<sup>-1</sup>; above this level solutions should be diluted. The calibration curve was constructed using a first-order regression fit of the data with peak area and ethanol concentration as axes.

The limit of detection for ethanol in alkaline solution, defined by a signal-to-noise ratio of 3, was 0.1 mg l<sup>-1</sup>. Typical chromatograms of blank and standard solutions are shown in Fig. 2.

### Derivatization and saponification procedure

This improved technique can be used to quantify super-absorbent polyacrylates in all workplace atmospheres tested. The ease of use makes the derivatization and saponification steps practical for routine sample analysis. Ethanol was chosen as the derivatizing reagent because it was completely removable after the esterification procedure and showed no interferences in the chromatograms of field samples as other alcohols did. It was found that complete evaporation of ethanol was possible only in quartz vials. Glass vials retained higher levels of ethanol on their walls. Using propan-1-ol, residual amounts were trapped on the walls of the reaction vials and in the filters, which could not be fully controlled. This resulted in an increase in the limit of detection for the polymer and the relative standard deviation.

Each step in the derivatization and saponification procedures was evaluated and optimized with regard to practical handling aspects. In all experiments the esterification factor, which represents the yield of esterification and hydrolysis, was determined.

By varying the composition of the esterification mixture it was observed that the presence of water was essential for the formation of the esters in sufficient yield. Minimum amounts of water are necessary for the swelling of the superabsorbent

**Table 1** Esterification factors (EF) of different particle size fractions of Sanwet IM 7100

Particle size fraction/ $\mu\text{m}$	Average EF ( $n = 3$ )
Micronized material	0.33
0–45	0.30
45–106	0.31
106–150	0.32
150–300	0.29

polyacrylate. This permits better diffusion of ethanol to the carboxylic groups located in the inner volume of the particles.

Regarding the saponification step, it was found that the hydrolysis yield reached a maximum and constant value if the Teflon filter was wetted with butan-1-ol prior to the addition of sodium hydroxide solution. The described reaction times and temperatures were found to be very suitable for obtaining reproducible results.

### Esterification factor

The esterification factor of the different product types tested was found to be in the range 0.20–0.35 with an RSD < 10%. For example, the EF for Sanwet IM 3900 was  $0.27 \pm 0.02$  and that for Sanwet IM 7100 was  $0.33 \pm 0.02$ .

The influence of particle size was tested with the SAP-type Sanwet IM 7100. The results (Table 1) showed that the particle size had no influence on the esterification factor of the product.

### Accuracy and precision

Blank Teflon filters were spiked with micronized Sanwet IM 3900 suspended in butan-1-ol. All samples were processed according to the described method. Ten repeated measurements at different levels of concentration produced average recoveries always higher than 85%. Because of the difficulty of spiking exactly the same amount of SAP on each filter the standard deviation was calculated on the basis of the variability of the recoveries at each level. The RSD was  $\leq 7\%$ . The results are given in Table 2.

### Limit of detection (LOD)

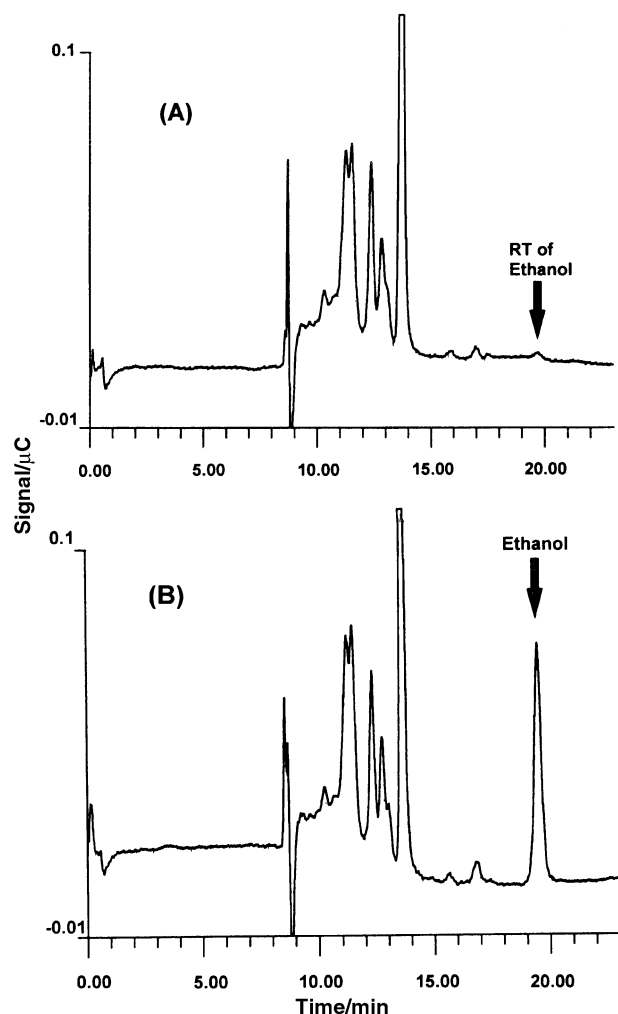
The LOD in this paper is taken as that concentration of ethanol which gives a result significantly different from blank Teflon

**Table 2** Recovery and precision data for Teflon filters spiked with SAP material Sanwet IM 3900

SAP spike level per filter/ $\mu\text{g}$	Range of SAP spiked/ $\mu\text{g}$	No. of values	No. of outliers	Range of SAP found/ $\mu\text{g}$	Range of recovery <sup>a</sup> (%)	Average recovery <sup>a</sup> (%)	RSD (%)
5	3.9–6.3	10	1	4.3–6.5	96–108	104	5.9
10	7.8			6.7	86		
	9.6			8.8	92		
	9.6			10.1	105		
	9.7			8.7	90		
	10.6	10	0	10.6	100	97	6.9
	10.7			10.3	96		
	10.9			10.6	97		
	8.8			9.3	106		
	9.1			9.5	104		
	10.8			10.4	96		
20	20.6–25.9	10	0	18.6–23.8	83–94	88	5.2
50	38.8–56.1	10	1	38.2–55.8	87–101	91	7.0

<sup>a</sup> The single values are presented only for the 10  $\mu\text{g}$  per filter level; all values are corrected by the filter blank.





**Fig. 3** HPLC traces for typical CTMP fluff sample processed according to the described method: (A) blank Teflon filter spiked with 0.6 mg of CTMP fluff; and (B) blank Teflon filter spiked with 0.8 mg of CTMP fluff and ethanol standard solution which corresponds to 0.020 mg of SAP per filter.

filters. The determination was based on (1) the analytical detection limit, (2) the variability of ethanol levels originated by blank filters and (3) the variability of repeated measurements of the same sample. The LOD was derived from three times the combined variability of (1)–(3).

The analytical LOD was  $0.1 \text{ mg l}^{-1}$ . The average ethanol concentration of blank Teflon filters was  $0.18 \text{ mg l}^{-1}$  with a variability of  $0.12 \text{ mg l}^{-1}$  ( $n = 20$ ). The standard deviation of repeated HPLC analysis of the hydrolysis solution of the same blank filter was  $0.05 \text{ mg l}^{-1}$ . The combined variability ( $s$ ) was calculated according to

$$s = (0.12^2 + 0.12^2 + 0.05^2)^{1/2} = 0.16 \text{ mg l}^{-1}$$

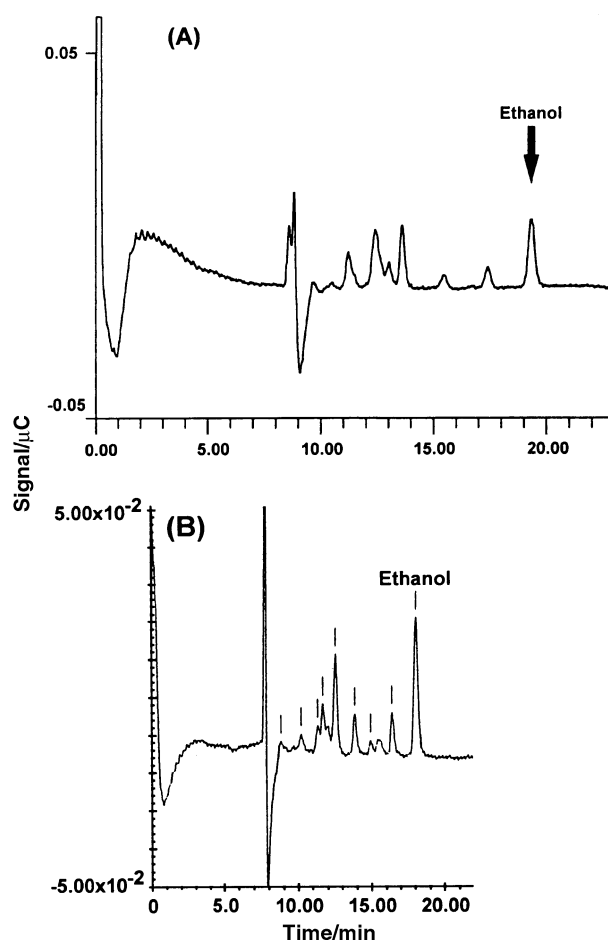
$$\text{LOD} = 3s = 0.49 \text{ mg l}^{-1}$$

Based on an esterification factor of 0.30 and an end-volume of 2 ml of hydrolysis solution, this value corresponded to  $3.3 \text{ } \mu\text{g}$  of SAP per filter.

For all sets of workplace samples the mean blank value for at least five blank Teflon filters was subtracted from each sample result to obtain a corrected level of SAP in each sample.

## Interferences

In plants converting SAP material, fluff is often used in the manufacturing process. Different bleached and non-bleached fluff types were examined for their ability to increase the filter blanks or to cause potential interferences in HPLC.



**Fig. 4** HPLC traces for workplace samples collected (A) in a SAP manufacturing plant, where the ethanol concentration corresponds to  $15 \text{ } \mu\text{g m}^{-3}$  SAP, and (B) at a diaper production line, where the ethanol concentration corresponds to  $8 \text{ } \mu\text{g m}^{-3}$  SAP.

**Table 3** Results for workplace samples taken in parallel at neighboring fixed points at different work shifts

Sampling location	SAP concentration/ $\mu\text{g m}^{-3}$		
	Sodium method <sup>a</sup>	Sodium background <sup>b</sup>	Derivatization–HPLC method
A	20	9	12
B	22	13	4
C	18	29	3
D	29	25	< LOD

<sup>a</sup> Values not corrected for the background. <sup>b</sup> Background samples were taken from outside the plant.

None of the tested fluff types showed any influence on the filter blank if the amount was  $< 500 \text{ } \mu\text{g}$  per filter. No interfering peaks near the retention time of ethanol were observed in the chromatograms in any case. A typical chromatogram is shown in Fig. 3.

## Workplace samples

The improved method could be used to quantify SAP respirable dust in all workplace samples tested. Representative chromatograms are shown in Fig. 4.

The advantages of the method were demonstrated with two sets of filter cassettes which were sampled in parallel at fixed points in a manufacturing plant. One set was analyzed according to the sodium method and the other as described above. The results

are summarized in Table 3. The observed high specificity, ease of use and low LOD make this derivatization–HPLC technique practical for routine sample analyses, especially where high sodium levels may contaminate the samples.

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