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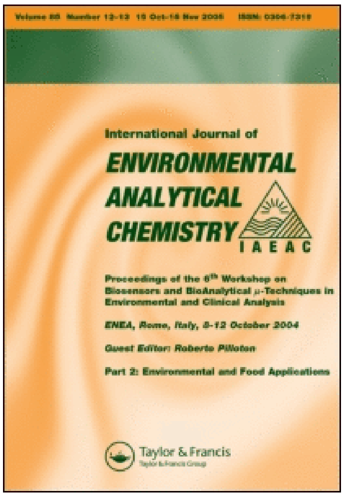

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Transesterification of Alkyl Acetates in Head Space Sampler†

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Environmental exposure of workers to organic solvents are routinely evaluated. Field samples are adsorbed on charcoal tubes and analysed by conventional GC or head-space (HS) GC. In the validation process of analytical protocols by HS-GC, it was observed that analysis of alkyl acetates yielded non-reproducible results when benzyl alcohol was used as desorbing solvent. Further studies by HS-GC with capillary column and GC-MS demonstrated a transesterification process of alkyl acetates. Reaction rate is dependent on steric hindrance of the acetate and on volatility of the newly formed alcohol. The presentation will describe some ways to obtain accurate and reproducible results. Data on environmental exposures of workers has been cumulated over two years in various industries involved in painting operations. Average worker exposure to aliphatic acetates will be discussed as well as other organic contaminants.

KEY WORDS: Environmental exposure, GC, (HS)GC, transesterification, aliphatic acetates, head space sampling alkyl acetates.

INTRODUCTION

A method using head-space sampling with gas chromatography (HS-GC) for the analysis of solvents in the workplace has been reported

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by several authors.[1–4] Field sampling is done by adsorption of volatile components on a 100 mg charcoal tube and desorption is carried out with benzyl alcohol. This method requires the use of a HS-GC equipped with a backflush system for the carrier gas to reduce time of analysis.

The method used in this study is similar, with the exception that a capillary column was used. The capillary column improves the chromatographic resolution and avoids the backflushing step. The equilibrium time and the temperature of the injector bath are two parameters that can strongly influence the reproducibility of the HS-GC analysis.[5] In some cases, chemical reactions may occur in the head space vial during or after the equilibrium time and may lead to systematic errors. The aim of this paper is to assess the systematic errors induced by the transesterification of alkyl acetates when benzyl alcohol is used as the desorbing solvent and to suggest some improvements for this analysis. Two years' cumulative data on environmental exposure of workers are presented.

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EXPERIMENTAL

Materials

Benzyl alcohol, benzene and acetates (methyl, ethyl, propyl (n- and iso-) and butyl (n-, sec-, iso- and tert-) from Aldrich were used in this study. Charcoal from charcoal tubes (100–50 mg, SKC, lot No. 120) was also used.

HS-GC and GC-MS conditions

HS-GC: F-45 Perkin Elmer with flame ionization detector
Injector: T° (bath): 70°C, T° (needle): 200°C, T° (injector): 210°C
Injection time: 5 s, split ratio: 1/20
Oven: T°: 130°C, 4 min, then 30°C/min, final T°: 190°C, 8 min
Column: SE-30, 50 m × 0.32 mm, d_f: 5 μm (Perkin Elmer Corp.)
Gas: Helium: 33 cm/s, Air: 300 mL/min, Hydrogen: 30 mL/min

Data handling was performed with a Varian CDS 401 integrator.

GC-MS: Finnigan 4500
Injector: T°: 210°C, split ratio: 1/40
Oven: 60°C, 2 min, then 20°C/min, final T°: 150°C, 3 min
Column: DB-5, 30 m × 0.25 mm, d_f: 0.25 μm (J. & W. Scientific Inc.)
Gas: helium: 34 cm/s
Ionizer: T°: 150°C
Electron energy: 70 eV
Emission current: 0.3 mA
EM: −982 V

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Procedures

Each solution of ester solvent was prepared by diluting the appropriate volume of the substance in benzyl alcohol containing the internal standard (benzene: 1.748 mg/mL of benzyl alcohol). The concentration of these solutions (Table I) corresponds to their respective threshold limit value[6] for a 10 L sampling volume.

TABLE I

Concentration of ester in Benzyl alcohol

Acetates	Concentration (mg/mL)	B.P.[a] (°C)
Methyl	6.125	64.7
Ethyl	12.86	78.3
n-Propyl	8.373	97.2
Isopropyl	9.457	82.3
n-Butyl	7.060	117.7
Isobutyl	6.968	107.9
Butyl (sec)	9.391	99.5
t-Butyl	9.284	82.5

[a] Boiling point of corresponding alcohols.

To reproduce the routine procedure of HS-GC analysis, vials containing 1 mL of solution and 100 mg of activated charcoal were prepared. These vials were sealed and placed in the isothermal bath of the HS-GC instrument. Head space samples were injected successively using the normal procedure, thus varying the equilibrium time of each sample. Results were also obtained with other samples that had specific and identical equilibrium time spans of 30 minutes before injection, by using the instrument on the "one-sample" injection mode.

RESULTS AND DISCUSSION

In the validation process of analytical protocols by HS-GC with capillary column, it was observed that successive injections of a calibration mixture of alkyl acetates yielded non-reproducible results when the equilibrium time was variable. This phenomenon was not due to an injection problem because results of peak areas of the internal standard were reproducible. It was also observed that the analytical precision was improved when the ester radical was bulky.

Figure 1 shows two chromatograms of a mixture of alkyl acetates and their corresponding alcohols at different equilibrium times. The appearance of these alcohols suggests hydrolysis or transesterification with benzyl alcohol. It is well known that transesterification occurs when an ester is heated with an alcohol in the presence of an acid or base. No reaction occurs without activated charcoal. In this case, activated charcoal seems to act as an acid catalyst. Table II shows kinetic parameters of the ester reactions for all the substances concerned in this study. The reaction constants are calculated (Table II) for each of the esters and are in agreement with the rules of the steric hindrance for classic of hydrolysis or transesterification reactions.[7] Further confirmation of transesterification is demonstrated in Figure 2 by the positive identification of benzyl acetate in a sample of ethyl acetate by GC-MS. Benzyl acetate cannot be analysed by HS-GC due to its low volatility. A chemical ionization technique with argon in SIM mode was found to be necessary in order to easily identify benzyl acetate in the presence of benzyl alcohol.

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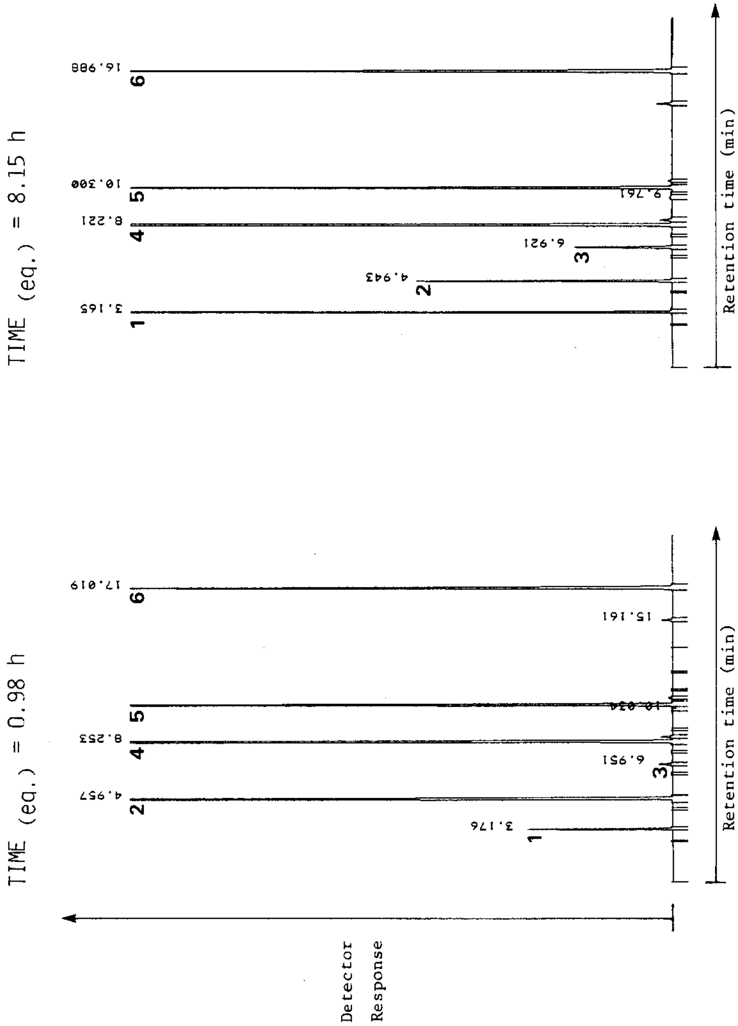

FIGURE 1 Chromatograms of two alkyl acetates at different equilibrium times (1 = Methanol, 2 = Methyl acetate, 3 = Isobutanol, 4 = Benzene (internal standard), 5 = Isobutyl acetate and 6 = Benzyl alcohol).

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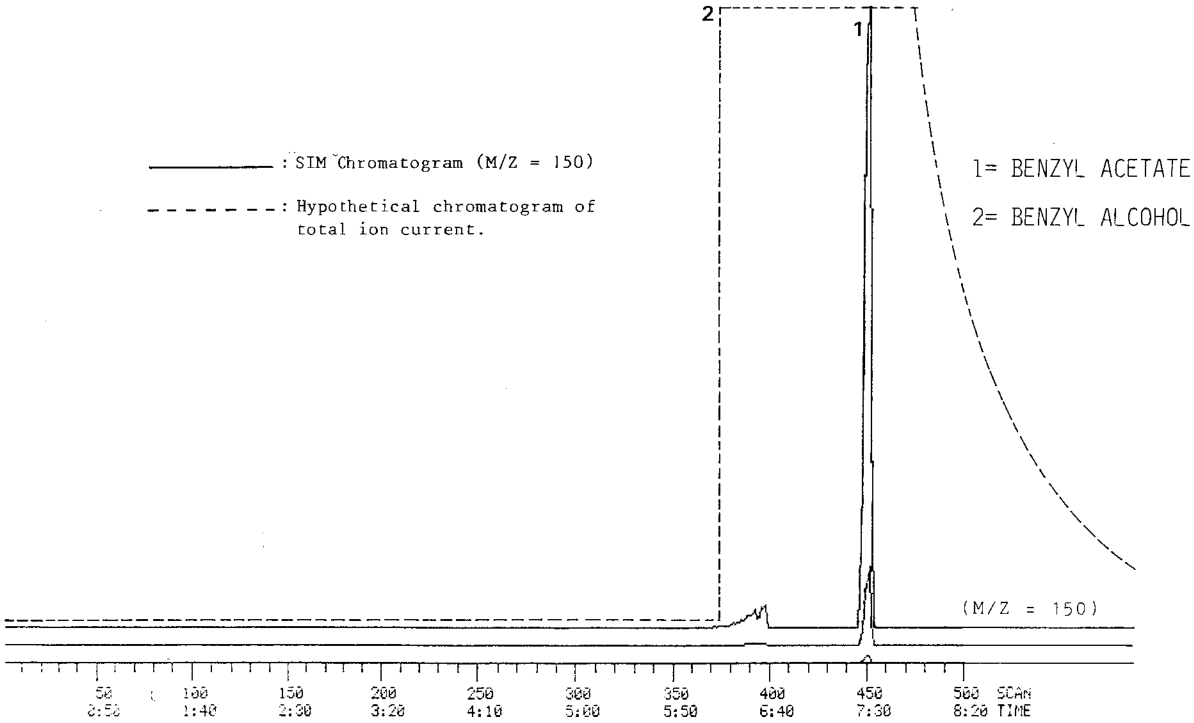

FIGURE 2 Confirmation of the presence of benzyl acetate by GC-MS.

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TABLE II

Kinetic parameters of transesterification at 70°C

Acetates	k transesterification (h^{-1})	$t\frac{1}{2}$ (h)	%[a]	r^b
Methyl	−0.226	3.06	12%/10 h	−0.992
Ethyl	−0.0626	11.1	59%/10 h	−0.976
n-Propyl	−0.0447	15.5	65%/10 h	−0.958
Isopropyl	−0.00543	127	96%/10 h	−0.961
n-Butyl	−0.0427	16.2	55%/14 h	−0.963
Isobutyl	−0.0262	26.4	70%/14 h	−0.993
Butyl (sec)	−0.00138	500	98.5%/17 h	−0.884
t-Butyl	≃0	∞	99.9%/17 h	—

[a] Percentage of ester unchanged after given times (h) in the bath.

[b] Coefficient of correlation of the log transform of concentrations of substances vs. time.

Under the conditions of this analytical procedure, the transesterification reaction follows first order kinetics (as demonstrated by values of the coefficient of correlation close to 1.00 in Table II) because of the large excess of benzyl alcohol. Based on the principle of chemical equilibrium in organic chemistry, transesterification reactions of acetates should be influenced by the respective volatility of the reactants and products, and by the steric hindrance of the ester radical. Since, in the present case, the presence of activated charcoal has been shown to be necessary to the reaction, a mechanism by acid catalysis at the surface of the adsorbent is strongly indicated. Such surface reactions are known to be sensitive to steric effect which is compatible with the results.

There are two ways to avoid errors due to the transesterification process, in occupational hygiene applications:

1) Equilibrium time may be kept constant and to a minimum. The reaction yield, being at this point very low, will not cause any substantial error, except for methyl acetate (Table III) and the inherent bias could be accounted for.

2) It is possible to calculate, by taking into consideration the stoichiometry of the reaction, the sum of the unchanged ester and the corresponding alcohol. The values calculated are not dependent

TABLE III

Reproducibility of the injection of alkyl acetates when the equilibrium time is constant at 30 minutes

Acetates	Mean concentration (mg/mL)	C.V.[a] n[b] (%)
Methyl	5.91	1.35
Ethyl	13.47	0.41
n-Propyl	8.39	0.51
Isopropyl	8.87	0.27
n-Butyl	7.18	1.40
Isobutyl	7.14	1.26
Butyl (sec)	8.87	1.29
t-Butyl	8.89	0.82

[a] Coefficient of variation (%).
[b] Number of measurements = 11.

TABLE IV

Reproducibility of the sum of the unchanged ester and the corresponding alcohol when equilibrium time is not constant

Acetates	Ester + alcohol (μ moles/mL)	C.V.[a] (%)
Methyl	82.0	0.49
Ethyl	149.4	2.35
n-Propyl	84.0	1.18
Isopropyl	97.4	0.49
n-Butyl	62.9	2.05
Isobutyl	62.4	1.83
Butyl (sec)	84.3	1.46
t-Butyl	80.6	0.94

[a] Coefficient of variation (%), $n = 29$ for all substances.

on equilibrium times and are also very reproducible for all the ester solvents used in this study (Table IV). It is thus possible to quantitate the ester solvent unless the corresponding alcohol is one of the contaminants of the workplace.

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Occupational exposure

The average exposure of workers to alkyl acetates is summarized in Table V. These data have been collected during the last two years in paint, furniture and shoe industries. Most operations are related to paint manufacture, application of varnishes or lacquers and gluing processes. In general, only 40% of personal samples have shown worker exposure above 1% of the TLV. Even in this 40%, an average value around 10% TLV gives a strong indication that worker exposure to alkyl acetates is low as judged from the TLV.

Some specific cases of occupational exposure to ethyl acetate are reviewed in Table VI. They are all related to some operations in

TABLE V

Average occupational exposure to alkyl acetates (1982–1984)

Acetates	Number of samples	Exposure > 1% TLV (%)	Averages mg/m^3
Ethyl	420	38	160
n-Butyl	119	54	57
Isobutyl	55	46	57
Isopropyl	20	25	22
Amyl	30	0	—
Cellosolve	40	41	85

TABLE VI

Specific occupational exposure (mg/m^3) to ethyl acetate

		Concentrations of other contaminants			
Industries	Concentrations	MEK	MIBK	Toluene	Xylene
Paint fabrication	707	1950	134	483	101
Paint fabrication	864	270	82	626	62
Lacquers mixing	121	464	60	328	—
Spray painting	128	6	17	79	—
Spray painting	72	—	74	250	—
Varnishing	20	35[a]	—	440[a]	36
Remover bottling	156	—	—	—	—

[a] Only one present

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paint manufacture such as the cleaning of mixers, varnishing and spray painting, "remover" bottling being the only example of simple exposure to ethyl acetate. The highest concentrations of ethyl acetate in air were equivalent to half the TLV and were accompanied by concentrations of toluene, 2-butanone and 4-methyl, 2-pentanone at the level of their TLV.

Alkyl acetates, by their toxicity and average concentrations in the working environment, are thus minor components of occupational exposure to organic solvents. Industrial hygiene could be effectively controlled by monitoring aromatic and ketonic compounds except in very specific industrial applications of alkyl acetates. Accurate determination of alkyl acetates is required for assessment of air quality in the development of biological monitoring programs for workers exposed simultaneously or consecutively to many solvents.

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CONCLUSION

The analysis of the ester solvents by HS-GC and desorption with benzyl alcohol may lead to significant errors. The use of capillary columns has permitted easy detection of the problem. However, it is still possible to analyze, with good reproducibility, the ester solvents by keeping the equilibrium time constant (now possible by using the new HS-GC[8]), by calculating the sum of the unchanged ester and its corresponding alcohol, or by changing the desorption solvent.

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