

# Gas chromatographic determination of some alkoxysilanes for use in occupational exposure assessment

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The manufacture and application of organosilicon compounds, especially silanes, have increased dramatically during recent decades. This has led to an increase in the number of exposed workers in different areas of industry. Therefore, there is an urgent need for an analytical method which can assess exposure to these compounds. A capillary column gas chromatographic (GC) method was developed for detecting 3-methacryloxypropyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane and 3-aminopropyltriethoxysilane. The silanes diluted in heptane were analysed by GC using flame ionisation detection. Gas chromatography–mass spectrometry was used to confirm the identity of the GC peaks. The analytical range of the method varied from 1 or 5  $\mu\text{g ml}^{-1}$  to 500  $\mu\text{g ml}^{-1}$  depending on the silane being studied. The detection limits were 1  $\mu\text{g ml}^{-1}$  for 3-methacryloxypropyltrimethoxysilane and 3-glycidoxypropyltrimethoxysilane and 5  $\mu\text{g ml}^{-1}$  for 3-aminopropyltriethoxysilane. The mean recovery of silanes tested with patch samples was >95% for all of the silanes. The repeatability of the patch sample method for silanes varied from 6.5 to 10.1%. This new GC method allows the simultaneous determination of three organosilicon compounds for occupational exposure assessment.

The most commonly used organic silicon compounds can be divided into siloxanes and silanes. Siloxanes are compounds which have a general silicon–oxygen–silicon backbone. The most important siloxane polymers are polydimethylsiloxanes, commonly known as silicones. These can be linear polymers with varying degrees of polymerisation or cyclic chains or rings. Organosilicon monomers (silanes) are composed of one or more silicon atom linked to hydrogen, nitrogen, halogen or some organic group. The variety and diversity of mono- and polysilanes are due to the great number of possibilities for combining substituents to the silicon. The organofunctional substituents often used with silanes are vinyl, methacryloxy, epoxy, sulfur, aminopropyl, ureic or isocyanato groups.

Although they have been known since the 1950s, the use of organosilicon compounds such as silanes has increased dramatically during recent decades. Organofunctional trialkoxysilanes of the general formula  $\text{RSi(OR)}_3$  are widely used as coupling agents for surface coatings and adhesion promoters of polymers to glass and metal surfaces. In glass-fibre production, propyl-trialkoxysilanes such as 3-glycidoxypropyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane and 3-aminopropyltriethoxysilane (Fig. 1) are used as agents binding the glass filaments and various resins in the primary production.<sup>1</sup> In hydrolysis, these silanes are partly transformed into analogous silanols which can readily form hydrogen bonds to water molecules adsorbed on an alloy (glass) surface. Side hydroxide groups become condensed, forming a siloxane network. The organofunctional end of the molecules, the methacrylate, epoxy or amino group, reacts with the resin and the organosilicon compounds effectively glue the resin to the glass filament. It has been previously estimated that the number of workers exposed to these three silanes increased from about 2000 in 1974 to over 130 000 in 1983 in the USA alone.<sup>2</sup>

Organic silicon polymers (silicones) have commonly been assayed using atomic absorption (AAS) or atomic emission spectrometry (AES).<sup>3</sup> This is based on the determination of elemental silicon but it gives no information on the structure of the siloxane(s) present. Instead, infrared (IR) and nuclear

magnetic resonance (NMR) spectrometric methods are generally used for both qualitative and quantitative analyses of siloxanes.<sup>3,4</sup> In order to separate and identify the many different organosilicon compounds present in the same sample, it is necessary to use chromatographic methods as reviewed by Steinmeyer and Becker.<sup>5</sup> However, only a few chromatographic methods, especially for trialkoxysilanes, have been published. Some of the recent studies on alkoxysilanes have dealt with NMR and IR spectrometric or gel permeation chromatographic methods.<sup>6,7</sup> According to Shatz *et al.*,<sup>8</sup> several gas chromatographic (GC) methods with different kinds of packing materials in packed columns have been developed for alkoxysilanes, but these are no longer acceptable. Mlejnek *et al.*<sup>6</sup> introduced a method for vinyltri(2-methoxyethoxy)silane using GC with a fused-silica wall-coated open-tubular (WCOT) capillary column. A liquid chromatographic method was recently published<sup>9</sup> for 3-glycidoxypropyltrimethoxysilane used as a fixing additive in silicone and polyurethane resins.

According to the current literature, there is no method available for the assessment of occupational exposure to

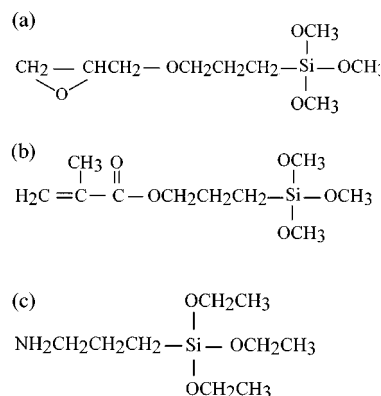


Fig. 1 Structures of (a) 3-glycidoxypropyltrimethoxysilane, (b) 3-methacryloxypropyltrimethoxysilane and (c) 3-aminopropyltriethoxysilane.

commonly used trialkoxysilanes either for biological monitoring of workers or for occupational hygiene measurements at the work site. The need for this kind of exposure assay has arisen from several recent case reports describing contact allergy in the glass filament and plastics industries.<sup>9–11</sup> The source of the contact dermatitis and sensitisation in the glass filament production was an amine-functional methoxysilane in two reported cases.<sup>10,11</sup> A worker in the plastics industry was found to be allergic to an epoxysilane, 3-glycidoxypropyltrimethoxysilane, which was contaminated with a reactive epoxy diluent.<sup>9</sup>

In occupational hygiene measurements, several kinds of sampling methods are available for determining the inhalation or dermal exposure to a certain chemical agent. For the assessment of exposure through inhalation, air samples are collected on adsorbents of different material or filters or in absorbent liquids. More emphasis has been placed on dermal exposure recently, since respiratory exposure has decreased owing to improvements in preventative measures, *e.g.*, better ventilation systems.<sup>12</sup> Collection of patch samples and hand-wash samples is a commonly used method for assessing dermal exposure, especially in pesticide research.<sup>13,14</sup>

The aim of this study was to develop a sensitive and reliable GC method for the three above-mentioned trialkoxysilanes commonly used in glass-fibre production. We hoped to develop an efficient analytical tool for exposure assessment of workers handling several coating chemicals, especially silanes, in primary glass filament production.

## Experimental

### Chemicals

The three trialkoxysilanes studied, 3-glycidoxypropyltrimethoxysilane (purity >98%), 3-methacryloxypropyltrimethoxysilane (>98%) and 3-aminopropyltriethoxysilane (>98 %), manufactured by (Witco Europe S.A. Geneva, Switzerland), were supplied by a local glass filament factory which uses these silanes as detachment agents in the coating of glass filaments. The solvent, heptane, was obtained from Merck (Darmstadt, Germany) and was of analytical-reagent grade.

### Samples

The validity of the method was tested with samples prepared under laboratory conditions where the three silanes were diluted with heptane in order to prepare the desired dilution series for GC analysis. Different concentrations of silane solutions were spread on  $\alpha$ -cellulose patches (10  $\times$  10 cm) which were extracted with 25 ml of heptane. The samples were then analysed by GC. The mean recovery of samples with the relative standard deviation (RSD) was calculated from five different concentrations in the linear analytical range. During validation of the method, we also tested methanol as the solvent but the recovery and sensitivity were better with heptane.

### Gas chromatography

The gas chromatograph was a Hewlett-Packard (Avondale, PA, USA) Model 5880-A with a flame ionisation detector (FID). A DB-5 capillary column was used (J&W Scientific, Folsom, CA, USA) (30 m  $\times$  0.32 mm id, film thickness 0.25  $\mu$ m). The injection volume was 1  $\mu$ l, the injector temperature was 220  $^{\circ}$ C and the splitless time was 0.5 min. Helium was used as the carrier gas at a flow rate of 1.5 ml min<sup>-1</sup> and nitrogen as the make-up gas at a flow rate of 20 ml min<sup>-1</sup>. The initial temperature of the oven was 80  $^{\circ}$ C, which was raised at a rate of

3  $^{\circ}$ C min<sup>-1</sup> to 150  $^{\circ}$ C then at 20  $^{\circ}$ C min<sup>-1</sup> to the final temperature of 250  $^{\circ}$ C, which was held for 3 min. The detector temperature was 250  $^{\circ}$ C.

### Gas chromatography–mass spectrometry

A Hewlett-Packard Model 6890 gas chromatograph equipped with a Hewlett-Packard Model 5973 mass spectrometer and a Hewlett-Packard Model 6890 autosampler was used. The oven temperature programming was identical with that for GC-FID. The column was the same DB-5 and the carrier gas (helium) flow rate was 1.0 ml min<sup>-1</sup>. The transfer line heater temperature was set at 280  $^{\circ}$ C. The ion source temperature was 200  $^{\circ}$ C and the electron energy was 70 eV. The injector temperature was 220  $^{\circ}$ C, the splitless time was 0.5 min and the injection volume was 1  $\mu$ l.

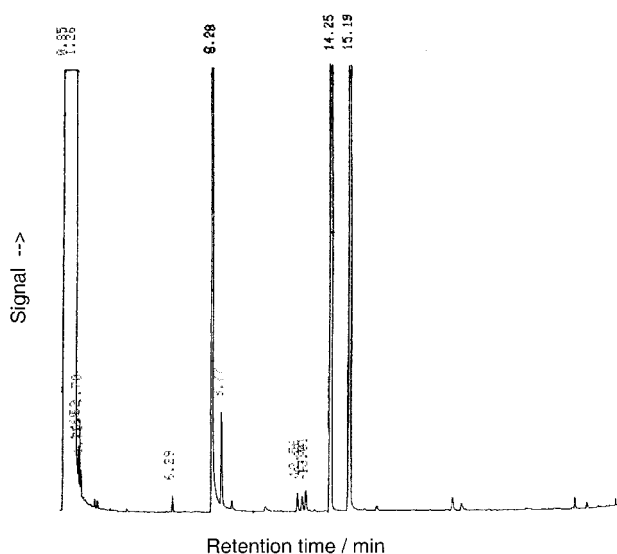
## Results and discussion

A method for the simultaneous GC determination of 3-methacryloxypropyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane and 3-aminopropyltriethoxysilane was developed (Fig. 2). The analytical range of the method for both 3-methacryloxypropyltrimethoxysilane and 3-glycidoxypropyltrimethoxysilane was 1–500  $\mu$ g ml<sup>-1</sup> with a detection limit of 1  $\mu$ g ml<sup>-1</sup>. The corresponding values for 3-aminopropyltriethoxysilane were 5–500 and 5  $\mu$ g ml<sup>-1</sup>. The mean recovery for occupational hygiene samples (patch samples) was 102% with an RSD of 2% for 3-methacryloxypropyltrimethoxysilane. For 3-glycidoxypropyltrimethoxysilane, the mean recovery for samples was 103% with an RSD of 3% and for 3-aminopropyltriethoxysilane the values were 100 and 5%, respectively.

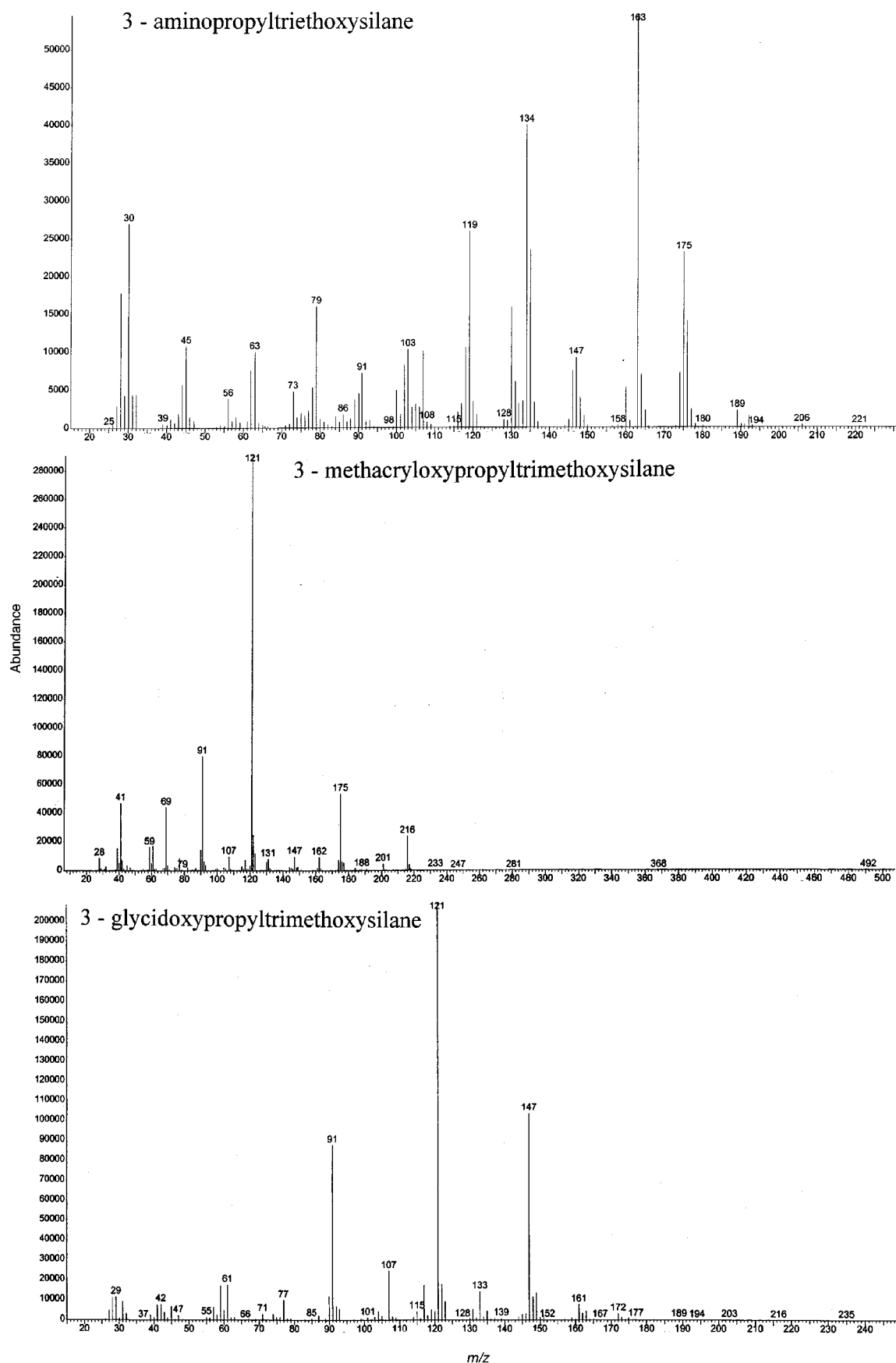
The GC peaks of the three silanes studied were verified by mass spectrometry. The identification of these silanes was based on the interpretation of the electron ionization (EI) mass spectra (Fig. 3).

The solvent experiments revealed that the use of heptane in the GC analysis improved the sensitivity compared with methanol (from 5 to 1  $\mu$ g ml<sup>-1</sup> and 20 to 5  $\mu$ g ml<sup>-1</sup>) depending on the silane tested.

The Dermal Exposure Network funded by the European Union is striving to develop a validated generic model of dermal



**Fig. 2** Gas chromatogram of 3-aminopropyltriethoxysilane, 3-methacryloxypropyltrimethoxysilane and 3-glycidoxypropyltrimethoxysilane. The retention times were 8.3, 14.3 and 15.2 min, respectively. The concentration of each silane was 50  $\mu$ g ml<sup>-1</sup>.



**Fig. 3** EI mass spectra of 3-aminopropyltriethoxysilane (top), 3-methacryloxypropyltrimethoxysilane (middle) and 3-glycidoxypropyltrimethoxysilane (bottom).

exposure for use in risk assessment. A number of models have been developed for specialist areas, *e.g.*, the occupational use of pesticides and the occupational use of industrial chemical compounds.<sup>15</sup> Validation of the models requires detailed

measurements of all aspects of exposure, including skin surface contamination surveys. The patch sampling method has been applied in assessing dermal exposure to pesticides and wood preservative agents studied in our laboratory.<sup>14,16</sup> Warm and

humid working conditions, the mode of exposure (splashing, contact) and the physical state of the chemical substance (aerosol) found in greenhouses and glass-fibre production are surprisingly similar, as seen in surveys concerning chemical and microbiological exposures and general working conditions.<sup>14,17,18</sup>

Our results showed that the GC-FID method developed for 3-methacryloxypropyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane and 3-aminopropyltriethoxysilane is sufficiently reliable for occupational hygiene measurements and evaluation of dermal exposure to these silanes from patch samples. With this method, one achieves equal sensitivities and linear analytical ranges for 3-methacryloxypropyltrimethoxysilane and 3-glycidoxypropyltrimethoxysilane and approximately the same reproducibility of parallel samples. The sensitivity for 3-aminopropyltriethoxysilane is slightly lower but nevertheless at the same level as for the other silanes. A lower detection limit could be achieved by concentrating the silane solutions *via* evaporation (to dryness) before the GC analysis, but we wanted to avoid any possible detachment of silanes from solid (glass) surfaces in case of unwanted hydrolysis. The volatilisation of the silanes during sample preparation is presumably negligible because of their low vapour pressure ( $<1$  mmHg).

The chemical heterogeneity of silanes poses challenges to analytical chemistry. In this work, the alkoxysilanes studied are similar in their chemical composition, all having the same propyltriethoxy or propyltrimethoxy structure. Nonetheless, these silanes show considerable differences in their physico-chemical features, *i.e.*, water solubilities and boiling-points. Special attention needs to be paid to avoid hydrolysis as the alkoxysilanes react readily with acids, bases or water (humidity). From a practical point of view, it will be a challenge to find an organic solvent suitable for the extraction of the organosilicon compounds, especially alkoxysilanes, and their metabolites from biological material.<sup>19</sup> Only a few studies have been published on the toxicological and environmental effects of organic silicon compounds, probably because of analytical difficulties in the determination of the dose.

In conclusion, a reliable and sensitive GC method was developed for the simultaneous determination of some alkoxysilanes commonly applied in glass-fibre production. This method will also prove useful in surveys to determine the amounts of organosilicon residues in the environment and to assess consumer exposure to personal care products such as

shampoos and hair conditioners containing organic silicon compounds.

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