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Determining Silanes in Inorganic Matrices by Pyrolysis - GC

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Abstract

Mineral building materials are normally treated with organosilicon compounds to make them hydrophobic. This article describes a pyrolysis-gas chromatography method for controlling the quality of surface protection. The method can be used to identify silanes and polysiloxanes as well quantify them if the appropriate calibrations have been made. During pyrolysis the organic material decomposes into the characteristic fragments, which can be determined by online gas chromatography. The method is reproducible within the tested parameters of pyrolysis with a relative standard deviation of less than 20%. The detection limit is about 0.05 wt.% silane.

Keywords: pyrolysis-gas-chromatography, methode of analysis, silane, siloxane

1 Introduction

The surfaces of mineral building materials can be protected by impregnating them with organosilicon compounds. In the presence of water, the silane forms hydroxyl groups that react with themselves to crosslink to polymeric networks or with hydroxyl groups on the inorganic surface (on the exterior of the building material or in the porous material) to anchor the hydrophobicizing groups chemically.

Water absorption can be used to test hydrophobicity. In addition to this general procedure, the pyrolysis-gas chromatography method described here makes it possible to detect the specific hydrophobicizing agent applied.

2 Pyrolysis-GC [1]

Pyrolysis is a powerful tool for providing unique information on the composition of non-volatile organic materials. Under conditions of thermal degradation, the organic chemicals decompose into the characteristic fragment patterns.

When polyorganosiloxanes are fixed in thermally inert inorganic matrices and pyrolyzed between 500 and 800 °C, the organoradical splits off in a matter of a few seconds and decomposes primarily into alkanes that have the same number of carbon atoms, e.g., propyltriethoxysilane splits mainly into propene, iso-butyltriethoxysilane (IBTEO) into i-butane, and n-octyltriethoxysilane (OCTEO) into n-octane (see figure 1).

The fragmentation pattern and the yield of the specific fragments depend on the nature of the inorganic matrix, which significantly influences the decomposition of the siloxanes on their surfaces, e.g., the octane yield in relation to the relative area of the that gc-peak decreases in the following order:

pure OCTEO > concrete > cristobalite (see figure 2).

The inorganic building materials are clean with respect to pyrolysis, which is easily controlled by analyzing a sample taken at a depth where silane has not penetrated. Until now, no interference with other chemicals (e.g., fluid aids, foam builders) has been observed. Their fragment pattern is indefinite and their concentration very low, so the pyrogram reveals only noise.

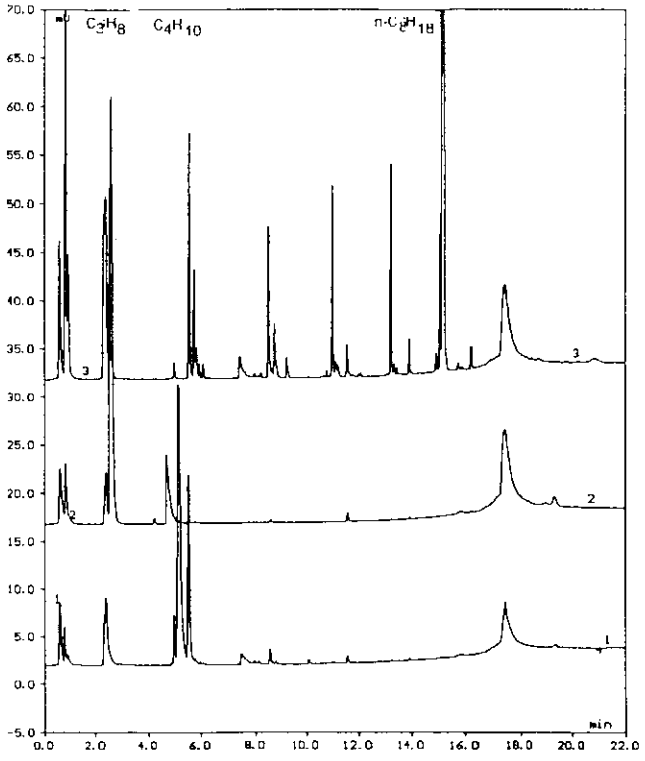

Figure 1: Pyrograms of concrete impregnated with different silanes: butyltriethoxysilane (1), propyltriethoxysilane (2) and octyltriethoxysilane (3)

3 Validation

Because the mechanisms and kinetics of this pyrolysis reaction are unknown, critical steps have to be controlled:

- the volatilization process, with the parameter of heat transfer depending on the masses of the inorganic material and the organic coating as well as pyrolyzer data
- and radical reactions in the carrier gas atmosphere, depending on fragment stability and concentration.

To check both of these situations, two calibration series were carried out.

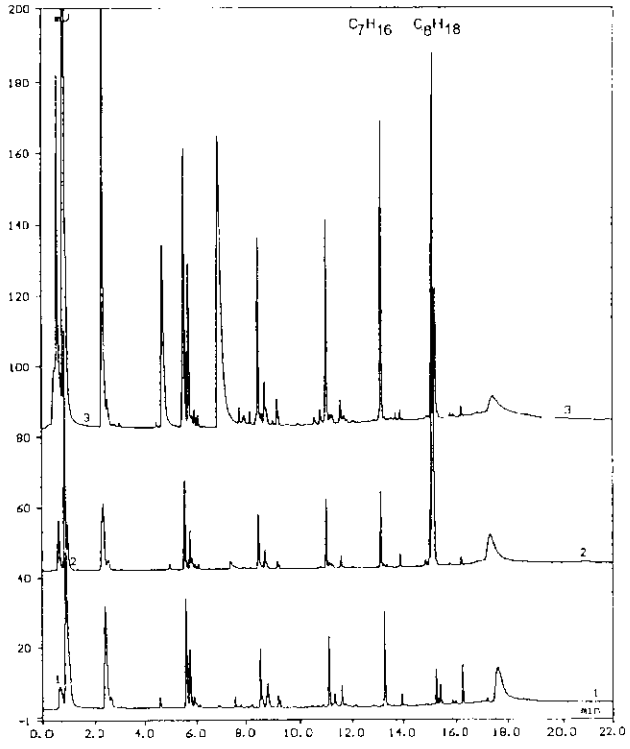

Figure 2: Pyrograms of pure octyltriethoxysilane (3) and different inorganic materials impregnated with octyltriethoxysilane: cristobalite (1), concrete (2)

In the first series, the sample weights for charging the furnace spanned over a large weight range. In the second series, the silane concentration varied over a large range, as described below:

- One sample of concrete having a definite concentration of isobutyltriethoxysilane (0.546 wt.% IBTEO) was analyzed nine times with different quantities of the specimen (0.15 to 5.25 mg concrete), with the equation of the calibration curve and the correlation coefficient as follows:

mass IBTEO(µg) = 2.032 x peak area (mV*min) + 1.15; r = 0.9966 (1)

- Three samples of concrete having different IBTEO concentrations (0.1, 0.5, and 1.0 wt.%) were pyrolyzed, with specimen quantities here covering a narrower weight range (1.3 to 4.6 mg concrete) and the equa-

tion of the calibration curve and the correlation coefficient as follows:

$$\text{mass IBTEO}(\mu g) = 2.285 \times \text{peak area.}(mV*min) + 0.61;\ r = 0.9988 \quad (2)$$

Both test series are cross-checked in such a way that the pyrograms of series 1 are calculated with the equation of series 2: The content of the single sample is verified with a mean of 0.564 wt.% IBTEO and a standard deviation of 0.067 wt.%. The detection limit is estimated on the basis of a signal/noise ratio of 0.05 wt.% IBTEO.

In the sample area investigated, which represents real concentrations after silane has been applied, pyrolysis-gc is a reproducible method, with the relative standard deviation being less than 20%.

4 Experimental Procedures

A furnace pyrolyser with a platinum sample cup was attached directly to a gas chromatograph equipped with a thin-film capillary and a flame ionization detector. The sample weight was less than 10 mg.

Samples were prepared from, e.g., cores taken from a controlled building. The sample powder is ground with a drill or a cutting disc or is filed by hand. The temperature during these procedures had to be below 150 °C to avoid uncontrolled thermal decomposition.

Calibration samples are prepared by impregnating standard concrete powder with the desired concentrations of the organosilicon compound under hydrolytic conditions and in sealed vials to avoid losses through volatilization.

Refernces

[1] Hüls AG, EP 0 741 293 vom 13.04.1995, *Verfahren zur Untersuchung silanbehandelter, anorganischer Materialien*