Application of the micro Raman spectrometer Mole to the analysis of thin layer chromatography fractions.

par J. v. Czarnecki et H. W. Hiemesch

(Materialprüfstelle der Bundeswehr, Erding, RFA)

Application de la microsonde Mole à l'identification semiquantitative des additifs des matériaux plastiques.

L'analyse d'un matériau plastique inconnu ou défectueux est souvent liée à la nécessité d'identifier des additifs tels que les stabilisateurs des antioxydants.

L'analyse classique, chromatographie liquide-spectrométrie de masse, ne peut généralement être appliquée car plusieurs additifs, souvent utilisés, ne pénètrent pas dans la colonne de séparation. Pour ce type de substances, la combinaison Mole-plaques CCM (plaques de chromatographie sur couches minces) offre une méthode rapide et assez simple pour l'identification semiquantitative.

La méthode proposée a été testée et utilisée avec des plaques CCM commerciales sans indicateur de fluorescence et avec la Mole dans un mode « image monocanal ». La zone intéressante des plaques CCM est illuminée avec un rayon laser défocalisé (diamètre d'environ 30 µ) utilisant un objectif de grande ouverture (× 100) et non le dispositif d'éclairement annullaire. Des substances peuvent ainsi être identifiées jusqu'aux concentrations inférieures à 10 µg dans le spot. Pour des concentrations inférieures à 50 µg (5 µg/mm), il est nécessaire d'utiliser une technique simple d'enrichissement pour obtenir un spectre identifiable. Des informations quantitatives et semiquantitatives peuvent être obtenues.

In our laboratory at the Material Testing Center in Erding, we developed a method to identify additives in unknown plastic samples by combining the capabilities of the Mole with thin layer chromatography (TLC). In general, the standard analysis GC-MS that is normally used cannot be applied because various substances often decompose below 350 °C, or because they have high boiling points and do not penetrate the gaschromatographic separation column. But the low concentration level of these highly effective additives in multicomponent mixtures requires a separation for detection and quantification. The TLC is the method used in such cases for its good separation performances, quantitative analysis capabilities, and ability to detect low concentrations of samples. In addition to these features, it is an inexpensive method and easy to use. However, since identifying substances in thin layer spots with reference plates, color reactions and covered distances proved time consuming and unreliable, a great deal of work was carried out to enable analysis of these spots by infrared spectroscopy. A good compilation of data in this respect was acquired by Grassili, *Progress in infrared spectroscopy*, vol. III (New York : Plenum Press, 1967). It is a quite complicated procedure to scrape the spot on the silica and then to enrich the substance in order to make it suitable for analysis in IR spectroscopy. Using micro-IR techniques, the empiracle detection limit is between 10 and 50 µg. A loss of substance caused by the transfer technique TLC-plate-KBr must however be considered.

Raman spectroscopy provides the simple possibility of analyzing these spots directly on the developed TLC plate, because silica is a poor Raman-scattering substance.

It is obvious that for the detection of low level concentrations, the TLC plate has to be free of any fluorescence indicator. For this purpose, we use the commercial plate Merck 5721 KG 50.

Because TLC fractions cannot be localized by fluorescence suppression in the uv light, we have made use of a reversible color reaction with iodation. The TLC plate is held in iodine vapor, whereupon a yellow-brown shading immediately occurs. The color reaction will normally disappear within a few minutes. This process can be speeded up in a heated drying oven. An increase of fluorescence caused by stable chemical reactions between the iodine and the adsorbed substance may at times persist. Therefore, it is frequently advised to develop different spots simultaneously using the same eluent solvent so that the covered distances will be equal and can be compared. After developing, one half of the TLC plate is protected by a glass plate and the other half is held in the iodine vapor, giving sufficient information regarding the position of all substance fractions on the protected side.

The lowest detection limit of a thin layer spot examined directly was specified at 10-50 µg/10 mm² spot area, which conforms to the Mole's 0.3-1 % detection limit of a substance in a mixture.

Thin layer spots of lower concentrations can be enriched for Raman-spectroscopic detection. The substance is eluted at the front of a solvent which is put on the TLC plate with capillaries at opposite sides of the spot. An enrichment factor up to 100 with resulting spot areas of typically 0.05-0.3 mm² can easily be attained. Using this technique, TLC spots below 1 µg can be detected.

Due largely to its high sensitivity and easy sample positioning, the micro Raman spectrometer Mole fully meets the requirements for examination of these small areas.

Quantitative results can be obtained by comparing the peak intensities in the spectrum with the covered TLC-spot areas. They are only semiquantitative because the concentration distribution is not uniform.

Our work specializes in the field of plastic additives, but this method can certainly be used in combination with other TLC applications.

Figure 1 shows the results of an analysis of a real polymer extract. The plasticizer is identified as Di(2-ethylhexyl) phthalat (c. reference
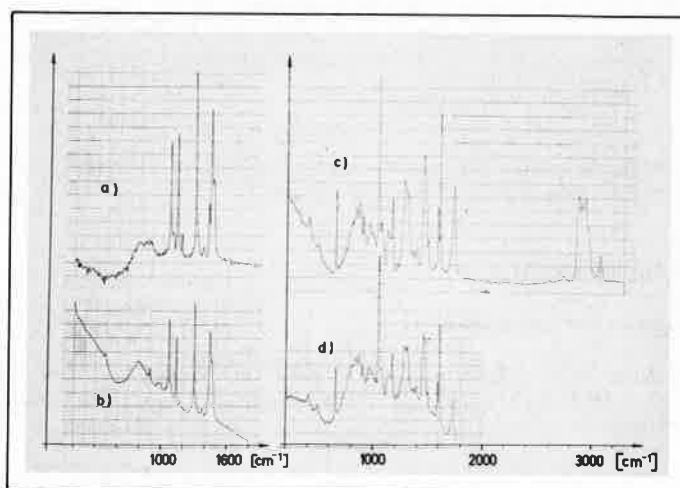

Figure 1.

spectrum, d. TLC spot). There is additionally an alkane in the extract that might be a low molecular polyethylene or a cristalline paraffin wax (b. TLC spot, a. reference spectrum of polyethylene).

The next extract (Figure 2) contains a paraffin oil made out of a foil of Opanol®. The sharp lines have disappeared (a. TLC spot, b. reference spectrum paraffin oil). The same plasticizer as in the first extract was used in this polymer (c). Di(2-ethylhexyl) phthalat is a product with a wide applications range.
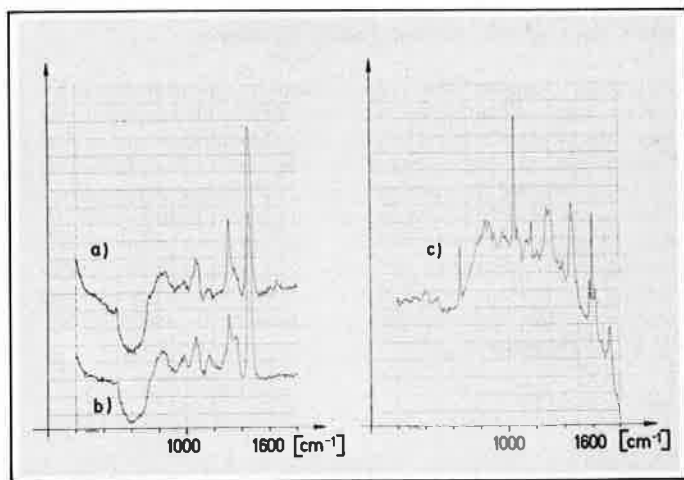

Figure 2.

The analysis of a waterhose is shown in figure 3. Besides the paraffin oil (e), Mesamoll® can be identified. The chemical formula is given. As it consists of molecules with different chain lengths $(CH_2)_n$ a thin layer chromatographic separation takes place. Having mainly used
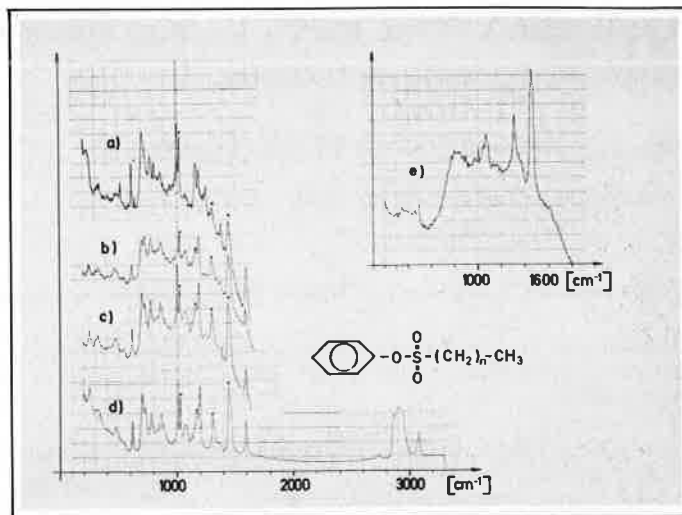

Figure 3.

petrolether as an eluent solvent, molecules with increasing chain lenghts therefore moved faster. Mesamoll® can be detected in different spots on the TLC plate (a-c. TLC spots, d. reference spectrum Mesamoll®). The changes in the spectra are caused by various chain lengths.

It has thus been shown that Raman spectroscopy with the Mole can be applied to the analysis of TLC fractions down to low concentrations. We believe it is a powerful and versatile tool highly suitable to use along with other techniques (GC-MS and IR). We will be adopting this method to study problems such as aging of additives, additives in oil and plastics, and extracts of matrix materials of unknown fiber compound preprags.

Some possibilities of Raman microprobe in cement chemistry

par M. Conjeaud et H. Jaeschke-Boyer *

*(Lafarge, Laboratoire de recherches, 78190 Trappes et * Jobin et Yvon, Laboratoire d'application, 91150 Longjumeau, France)*

Quelques possibilités de la microsonde Raman en chimie des ciments.

La microsonde Raman a été utilisée avec succès pour obtenir les spectres Raman in situ de cristaux d'alite et de bélite dans deux clinkers industriels. Des différences importantes ont été observées, et celles-ci sont comparées à la composition chimique de ces alites et bélites donnée par la microsonde électronique.
L'étude des deux autres phases des clinkers (C_3A et alumino-ferrites de calcium) et celle de l'hydratation ont été abordées. L'application de

la microsonde Raman pour le C_3A et les alumino-ferrites de calcium semble peu intéressante (du fait de l'influence néfaste du fer présent dans le C_3A des clinkers). Par contre, malgré les difficultés rencontrées dans l'étude de l'hydratation, les quelques résultats obtenus montrent que la microsonde Raman devrait permettre d'obtenir des informations sur les hydrates formés lors de la prise des ciments qu'aucune autre méthode ne peut fournir.

This paper relates the results obtained in cement chemistry and published in a cement specialized review (1).

Expérimental

Samples and preparation

Small samples (100 mg are largely sufficient) of pure C_3S, β-C_2S, C_3A, C_6A_2F, C_6AF_2 and C_2F * were prepared by high temperature synthesis.

For β-C_2S only, 1 % B_2O_3 by weight, was used as a stabilizing agent.

* $C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $F = Fe_2O_3$

Two industrial clinkers were studied : one a special white cement clinker, the other ordinary portland cement clinker.

In order to be able to obtain Raman spectra of alite, belite **, C_3A and calcium aluminoferrite in these clinkers, polished sections were prepared.

In order to study calcium silicate hydrate (C-S-H) three types of samples were prepared :
1. synthetic C-S-H (1) at C/S = 1 obtained by chemical reaction in solution between Na_2SiO_3 and CaO, and extensive washing to eliminate Na_2O (< 1 % by weight remaining).

** *alite and belite are the name given respectively to the impure C_3F and C_2F present in a clinker.*