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Hazardous compounds, electronic scrap materials, used cars, the EDX series from Shimadzu can detect "the ususal suspects" lead, chromium, cadmium, mercury and bromine according to Electrical and Electronic Equipment Act – ElektroG.

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Telefax: +49-203-766625
Email: shimadzu@shimadzu.de
Internet: www.shimadzu.de

Editorial Team:
Uta Steeger · Phone: +49-203-7687-410
Ralf Weber, Angela Baehren

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Plastic ducks banned from the bathtub?

Pyrolysis GCMS detects phthalic acid esters

Phthalic acid esters are widely distributed in our environment. They can be found in food, drinking water and many plastic objects that we use every day. Phthalates are used mainly as chemical plasticizers in the manufacture of plastics. They make plastic materials elastic and smooth, while preventing breaking or splitting of the material. The amount of phthalates used can vary widely; up to 40 % can be found in some plastic products. Since phthalates act as so-called external plasticizers – meaning they are not covalently bound to the plastic material – they can relatively easily be re-dissolved from the plastic. Additives not covalently bound can also "migrate" through the material, resulting in increased concentrations at the surface.

Plasticizers are also used to a lesser extent in quite different areas, for example as solvents and lubricants in industry or as carrier substances in deodorants and perfumes. They also can be found as permitted supplements in pharmaceutical products. For example, di-n-butylphthalate (DBP) is often used as an additive in capsules to make them resistant to gastric juices. The 2005 Red List (German list of pharmaceutical products) lists 64 preparations containing DBP. In PVC-based materials such as infusion containers of tubing systems, diethylhexylphthalate (DEHP) is very difficult to replace with alternative materials.

EU ban on plasticizers in toys

For some years, phthalates have been suspected of being carcinogenic, teratogenic and of acting as endocrine disruptors. The toxic effects of these compounds on the development and reproduction of organisms are at the center of current discussion. Already since the late 1990s, environmental toxicologists and consumer protection groups are fighting for a strict regulation and limitation of the use of phthalates. In 1999, a EU-wide preliminary ban on the use of plasticizers in babies' toys was issued and has been renewed each year since then.

The European parliament has now agreed on a EU directive banning the use of six of the phthalate esters in babies' toys; the ban also applies to imported goods. Under this ban, compounds such as DEHP, DBP and BBP (butylbenzyl phthalate), officially considered to be teratogenic, may no longer be used in toys. The use of plasticizers DnOP (di-n-octylphthalate), DiNP (di-iso-nonylphthalate) and DiDP (di-iso-decylphthalate) is forbidden in toys which children may put into their mouth. However, this regulation does not prevent little children putting the toys of their older siblings into their mouths.

Fast and reliable: Pyrolysis-GCMS

Determination and quantitation of plasticizers presents no prob-

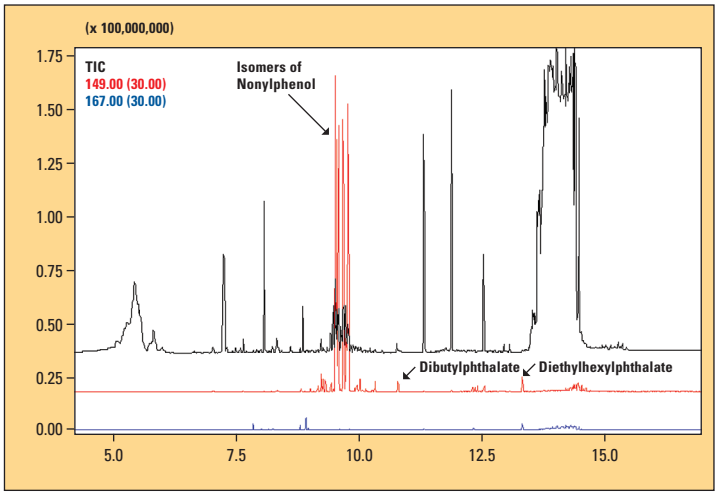

Figure 1: Chromatogram of the plastic duck sample with characteristic masses m/z 149 and 163 for the plasticizers. The fragment m/z 149 is also specific for nonylphenol and derivates of nonylphenol.

lem for the analytical chemist. HPLC and GC are classical methods for the determination of plasticizers. However, a disadvantage of these methods is the sample preparation required prior to analysis. Normally, this requires extraction of materials for several hours using a suitable solvent.

In some cases, the extract has to be further purified since plastic components may also dissolve, depending on the type of extraction solvent used, and interfere with the subsequent analysis. Another problem in sample preparation is posed by the plasticizers themselves. Due to their wide distribution, plasticizers are found all over the laboratory, for example in all kinds of solvents, and can therefore be carried over into the samples prior to analysis.

Pyrolysis GCMS is a fast and reliable alternative. This highly accurate analysis method requires no sample preparation and can be employed as a straightforward screening method for monitoring the six banned phthalates.

In order to perform the pyrolysis, a small piece of the sample to be analyzed, approximately 150-300 µg, is placed in a steel sample cup. The sample is heated in a pyrolysis oven under inert gas. The gaseous pyrolysis products are transported by a carrier gas stream to the analytical column of the gas chromatograph. The separate sample components are isolated and subsequently detected and identified using a mass spectrometer.

As the plasticizers are not covalently bound to the plastic material, they can be evaporated at a relatively low temperature. At these low temperatures neither the phthalates nor the plastic materials will degrade. Since only few matrix components are desorbed, the phthalates can readily be separated and detected. In this way, even low amounts of phthalates can be detected.

No more fun in the bathtub?

Using the analytical method described above, random samples from babies' and children's toys collected from the toy department of a major retail store were investigated. The three random samples comprised of a plastic duck, a plastic book and plastic ribbons currently in fashion with teenagers.

First, an aliquot of the plastic duck was analyzed since the baby toy was labelled as "non-phthalate containing". Figure 1 shows the chromatogram obtained at a desorption temperature between 100 °C and 300 °C. In fact, only traces of plasticizers can be found in the chromatogram of the sample, characterized by the mass traces m/z 149 and m/z 163.

However, the plastic book sample clearly showed the presence of plasticizers. The desorption chromatogram is shown in Figure 2. The plasticizers elute at 10.3, 10.8 and 13.35 minutes.

It is well known that the colorful plastic ribbons used by teenagers to make bracelets contain plasticizers. The packages are labelled with a warning indicating that the ribbons must be allowed to evaporate their fumes prior to use and, furthermore, that the ribbons should not be put in the mouth. This warning is certainly justified since the ribbons contain large amounts of the banned plasticizers, as can be seen in Figure 3, and do not belong in the hands of small children.

The Pyrolysis GCMS system is well suited to rapid and accurate determination of phthalates. The great advantage of this method lies in the simple and fast sample preparation method since only a minute amount of the sample needs to be cut out and used for the analysis. For this kind of analysis it is essential to measure blank samples at regular intervals in order to ensure that plasticizer

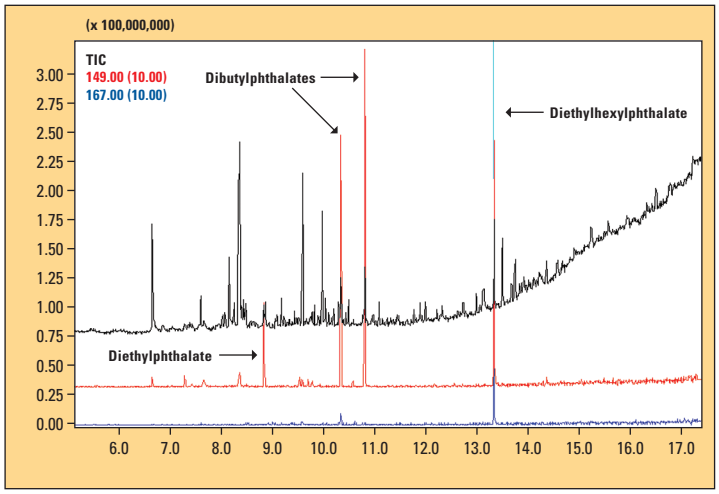

Figure 2: Phthalic acid esters found in samples isolated from the plastic book with their characteristic masses m/z 149 and 163

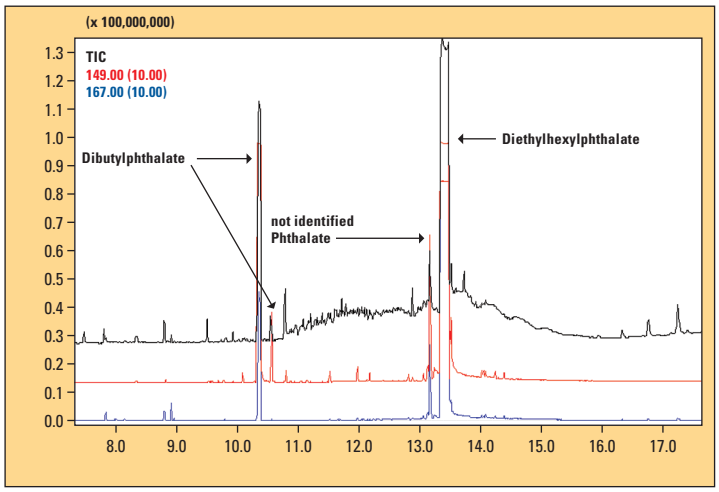

Figure 3: Phthalic acid esters found in plastic ribbons with their characteristic masses m/z 149 and 163

peaks are not caused by memory effects of previously analyzed samples.

The distinction between DEHP and DnOP as well as between di-butylphthalate, di-iso-butylphthalate (not affected by the ban) and DBP, cannot be performed simply via analysis of their mass spectra, since these compounds represent stereoisomers with virtually identical fragmentation patterns. An unambiguous identification can only be performed using appropriate standards.

Reference:

www.arbeitsmedizin.uni-erlangen.de/Koch_Phthalate.htm