

Successful participation in round robin tests

TOC suspension method for sediments and soils



Figure 1: Obtaining of sediment samples from a harbor basin carried out by the German company Schreiber in Duisburg

In accordance with the German AbfAbIV Waste Disposal Directive [1], disposal of wastes containing more than 1 mass% (Landfill class I) or 3 mass% (Landfill class II) of organic compounds is prohibited without thermal or mechanical-biological treatment. This also applies to wastes such as soils, sediments or construction waste.

As a direct consequence, the analytical requirements with respect to the TOC parameter (Total Organic Carbon) have increased dramatically. Due to its high degree of automation and low operating cost, the determination of TOC is currently the analytical

method of choice for the sum parameter determination of organic compounds. Using the new suspension method, solid samples such as sediments and soils can now be analyzed with considerably reduced expenditures in time and costs.

Suspension method

The suspension method was successfully applied to the pre-treatment of several matrices originating from the cement industry [3]. Preparation of suspensions from sediments and soils requires optimization of the sample preparation procedure. The sample material is finely pulverized (< 200

µm) using appropriate grinding methods (for instance a ball mill) and is subsequently suspended in a dilute hydrochloric acid solution.

It is especially important to minimize re-sedimentation of the suspended particles. Particles are effectively homogenized using a suitable dispersion tool such as Ultraturrax®. TOC determination of the suspension is carried out via the NPOC method (Non Purgeable Organic Carbon). The IC (Inorganic Carbon) is quantitatively removed using acidification. Volatile organic compounds can be neglected (drying at 105 °C). For this application the following assumption therefore applies: NPOC = TOC.

Analytical system

TOC measurements on suspensions were carried out using a Shimadzu TOC-V_{CPN} including an ASI-V autosampler (Figure 2). The system works according to the catalytic combustion principle. Due to an optimized sample introduction technique employing the ISP module (Integrated Sam-



Figure 2: TOC-V_{CPH} with autosampler

ple Pretreatment), suspensions can be ideally quantified using this system.

Results from round robin tests

In addition to extensive comparative measurements [4], in part carried out using reference materials (see example in Figure 3), the suspension method was also tested by participation in two round robin tests.

The round robin tests involved ISE 2005.4 (International Soil-analytical Exchange Programme) and SETOC 2005.4 (Sediment Exchange for Tests on Organic Contaminants) coordinated by WEPAL (Wageningen Evaluating Programmes for Analytical Laboratories) in Wageningen, the

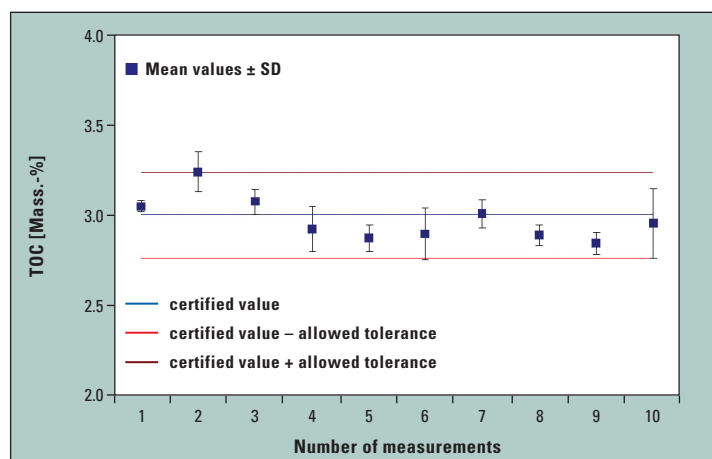


Figure 3: TOC suspension measurements using Reference Standard NIST41b

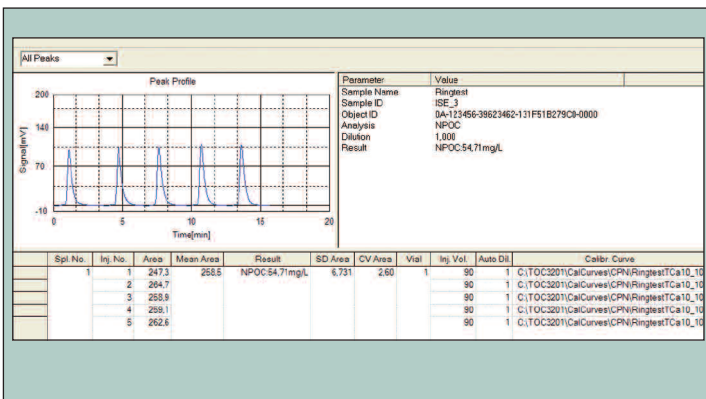


Figure 4: NPOC determination of a suspension sample

Netherlands. Each participating laboratory received 4 soil and sediment samples for testing. Figure 4 shows a NPOC determination of a suspension sample.

Three participants in the round robin tests have determined the TOC values independently of each other using the suspension method:

1. Laboratory for water analysis, Umweltbundesamt (Federal Environmental Agency) in Berlin, Germany
2. ALBO-tec GmbH, Technology Centre for Analysis and Soil Mechanics in Bochum, Germany
3. Shimadzu Europa GmbH in Duisburg, Germany.

Figure 5 shows an overview of the round robin test results of the suspension method compared with the overall result.

The median is based on the results of the round robin tests and the amount of relevant participants (ISE: 24 - 29; SETOC: 12 - 15). The results of the participants in 'Lab 1, 2 and 3' were obtained using the suspension method.

Good day, sunshine

Simultaneous detection of UV filters in sunscreen

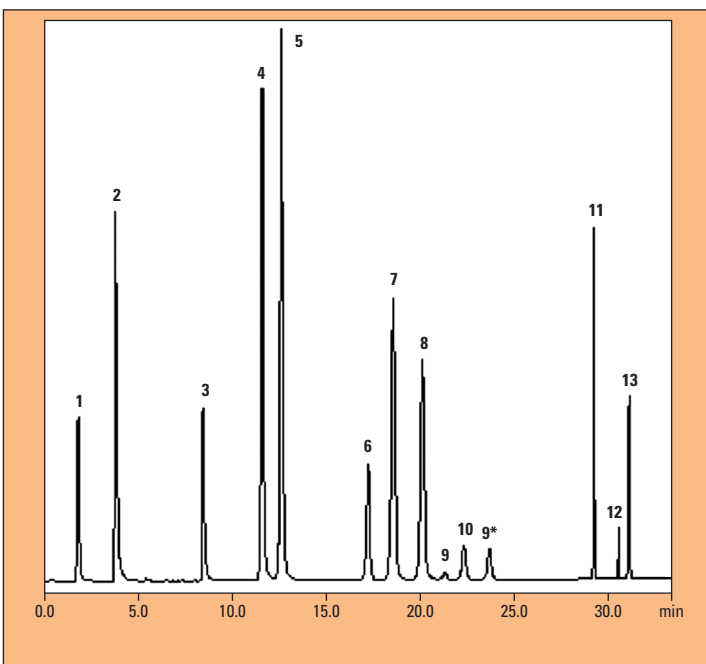


Figure 1: Typical chromatogram of the developed method, with thirteen UV filters separated in one run

When visiting the beach or walking the hills on a sunny summer day, people often apply sunscreen lotions. These are developed to protect our skin by reflection or absorption of solar radiation using UV filters, allowing us to stay longer in the sun.

UV rays are divided into three major groups:

- UVA rays of long wavelengths (380 – 315 nm)
- UVB rays of medium wavelengths (315 – 280 nm) and
- UVC rays of short wavelengths (< 280 nm).

In contrast to UVA and UVC rays, UVB rays cause sunburn of the skin.

Although UV filters have a protective function, their levels in cosmetic products are regulated by the European Union. In order to determine the levels of UV filters within sunscreens, assays have been set up to qualify and quantify these UV filters using liquid chromatography and gas chromatography [1,2].

Several methods for the simultaneous determination of several UV filters using a polymeric bonded silica ODS type reversed phase column are to be found in the literature.

This application describes a method for the simultaneous

determination of thirteen internationally authorized organic UV filters commonly found in sunscreen products. For the separation, a Pathfinder MR column (polymeric encapsulated silica based, reversed phase) was used.

The filters determined were:

- 4-amino-benzoic acid (PABA)
- benzophenone-3 (Benz-3)
- 2-phenylbenzimidazole-5-sulfonic acid (PBSA)
- homosalate (HMS)
- 2-ethylhexyl-4-dimethylaminobenzoate (ED-PABA)
- 2-ethylhexyl-4-methoxycinnamate (EMC)
- drometrizole trisiloxane (DTS)
- isoamyl-p-methoxycinnamate (IMC)
- ethylhexyltriazone (ET)
- 2-ethylhexylsalicylate (ES)
- diethylhexyl butamido triazone (DBT)
- octocrylene (OC)
- 4-methylbenzylidene camphor.

The measurements have been carried out using a *prominence* HPLC system with PDA detection.

Conclusions

In addition to savings in time resulting from the straightforward sample preparation process and thorough automation via the ASI-V, the suspension method offers high analytical accuracy based on the multiple-injection requirement under AbfAbfV. Measuring errors due to contamination are reduced considerably. An additional solid sample module is no longer necessary. This leads to a reduction in acquisition costs.

- [1] Verordnung über die umweltverträgliche Ablagerung von Siedlungsabfällen (BGBl. S. 305; 24.07.2002, S. 2807) (Ordinance on Environmentally Compatible Storage of Waste from Human Settlements and on Biological Waste-Treatment Facilities)
- [2] Verordnung über die Verwertung von Abfällen auf Deponien über Tage (BGBl. Nr. 46 vom 28.07.2005, S. 2252) (Ordinance relating to the recovery of waste at surface landfills and amending the Commercial Wastes Ordinance)
- [3] TOC in der Zementherstellung (LABO 12/2004)
- [4] Der TOC in Sedimenten und Böden – Fortschritte in der Analytik (WLB 10/2005)

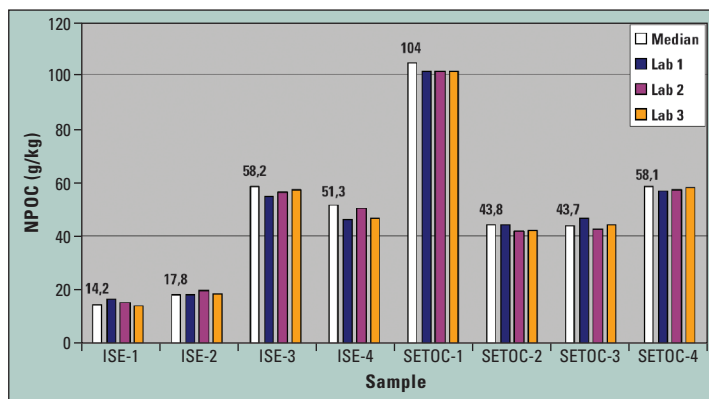


Figure 5: Round robin test ISE 2005/4 and SETOC 2005/4 (WEPAL, Wageningen, NL)

products

Nr.	Compound	k'	Resolution
1	PABA	0.2	
2	PBSA	1.5	10.2
3	Benz-3	4.6	26.9
4	IMC	6.7	16.2
5	MBC	7.3	4.4
6	OC	10.4	17.3
7	ED-PABA	11.3	4.2
8	EMC	12.3	4.6
9	HMS	13.1	3.3
10	ES	13.8	2.6
9*	HMS	14.7	3.5
11	DBT	18.4	23.8
12	DTS	13.2	14.9
13	ET	19.7	5.0

Table 1: Overview of the UV filters in the chromatogram, with retention factors and resolutions

Figure 1 presents a typical chromatogram of the developed method, where thirteen UV filters are separated in one run. The similar chromatographic properties of the compounds makes it difficult to obtain a complete baseline separation of all thirteen compounds. With the described method, it is possible to resolve all of the UV filters. Resolution of all pairs is larger than 1.5, as can be seen in Table 1. This allows accurate qualification and

quantification of UV filters in sunscreens. The two peaks observed for HMS are typical for this compound, since HMS is present in two isomers forms [4].

In contrast to the method developed by Schakel and co., a selectivity difference occurs between the LiChrospher® column used in their method and the Pathfinder column used in this study. The difference can be explained by the fact that Pathfinder can be catego-

rized within the family of polar embedded reversed phase columns [5]. Apart from the hydrophobic interaction model, playing a major role within regular ODS types of columns, Pathfinder alters selectivity due to the polar groups incorporated in the structure. In cases where matrix peaks disturb the analysis, selectivity change with polar embedded columns can be a good alternative.

An additional benefit of Pathfinder columns over regular ODS phases: there is no need to add base deactivating products such as EDTA, as described in a previous study [3], in order to obtain reasonable peak shape. The polymer shield around the silica core prevents analytes interacting with residual silanols.

With the present method it is possible to separate 13 of the most common UV filters found in sunscreen products. The method can be used as an alternative to existing methods when alternative selectivity is desired.

The development of this application was accomplished in cooperation with the research lab for non-food chemicals of the Food and Consumer Product Safety Authority, Groningen, the Netherlands.

References

- [1] S. C. Rastogi and G. H. Jensen J. Chromatogr. A, 828, 1-2, 18 Dec. 1998, 311-316
- [2] Kazuo Ikeda, Sukeji Suzuki and Yohya Watanabe J. Chromatogr. A, 513, 1990, 321-326
- [3] D.J. Schakel, D. Kalsbeek, K. Boer, J. Chromatogr. A, 2004, 1049, 127-130
- [4] A. Chisvert, M.C. Pascual-Marti, A. Salvador, J. Chromatogr. A, 921 (2001) 207
- [5] J. Layne, J. Chromatogr. A A, 957 (2002) 149 164