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Determination of SCCP and MCCP in different matrices by use of GC-ECNI-MS V8 final 20171117

1 Introduction

This working draft combines the input from CADS SCCP Working group 2014 to 2017 with different lab representatives and the Leather standard ISO/FDIS 18219:2014

2 Scope

Determination of SCCP and MCCP in different matrices by means of GC-ECNI-MS and solvent extraction.

3 Normative references

Principle was described in ISO/FDIS 18219:2014. The procedure of the standard method was changed in the following points:

- Widening the scope for MCCP, inclusion of four ion-traces
- Widening the scope by inclusion of other matrices than leather, e.g. polymers, coatings, man-made fabric, for this toluene should be used as extraction solvent (ref. to AfPS document for PAH)
- Adding clean-up procedure with sulfuric acid
- Lindane was defined as internal standard

4 Principle

Extraction of polymer samples, coated textile, printed textile and coated leather samples with toluene and uncoated leather samples with n-Hexane according to DIN EN ISO 18219, subsequent measurement by GC-NCI-MS. For SCCP and MCCP, respectively, 4 masses should be integrated.

The quantification ions and chlorination degree of the quantification standards were chosen by means of LC/ToF. Several real-life samples were screened and the average degree of chlorination was determined.

It has to be emphasized, that this method is a conventional method, all steps have to be performed as described.

5 Apparatus and materials

Normal laboratory apparatus, in particular the following:

- **Analytical balance**
- **Tight sealable vessel**, with lid, 20ml, suitable for solvent extraction and sulfuric acid- clean up (if applicable)
- **Ultrasonic bath** (temperature controlled)
- **PTFE membrane filter**
- **GC/ECNI-MS System**

6 Chemicals/Calibration

Unless otherwise stated, analytical reagent grade chemicals shall be used

- **n-Hexane**
- **Toluene**
- **Lindane (Internal standard)**
- **concentrated sulfuric Acid**
- **Standard solution**
- **SCCP 55,5 % Cl technical grade**, c = 100 µg/ml
- **SCCP 63 % Cl technical grade**, c = 100 µg/ml
- **MCCP 52 % Cl technical grade**, c = 100 µg/ml
- **MCCP 57 % Cl technical grade**, c = 100 µg/ml

Note: These standard solutions are commercially available e.g at LGC.

6.1 Preparation of SCCP calibration solutions with 59 % chlorination degree

6.1.1 Calibration solution 1 (5 µg/ml)

Transfer 53,3 µl of SCCP 55,5 % Cl standard solution and 46,7 µl SCCP 63 % Cl standard solution into a 2 ml volumetric flask. 40 µl of internal standard solution is added and the flask is filled to the mark with n-Hexane.

6.1.2 Calibration solution 2 (50 µg/ml)

Transfer 533 µl of SCCP 55,5 % Cl standard solution and 467 µl SCCP 63 % Cl standard solution into a 2 ml volumetric flask. 40 µl of internal standard solution is added and the flask is filled to the mark with n-Hexane.

6.1.3 Calibration solution 3 (75 µg/ml)

Transfer 800 µl of SCCP 55,5 % Cl standard solution and 700 µl SCCP 63 % Cl standard solution into a 2 ml volumetric flask. 40 µl of internal standard solution is added and the flask is filled to the mark with n-Hexane.

6.2 Preparation of MCCP calibration solutions with 55 % chlorination degree

6.2.1 Calibration solution 1 (5 µg/ml)

Transfer 40 µl of MCCP 52 % Cl standard solution and 60 µl MCCP 57 % Cl standard solution into a 2 ml volumetric flask. 40 µl of internal standard solution is added and the flask is filled to the mark with n-Hexane.

6.2.2 Calibration solution 2 (50 µg/ml)

Transfer 400 µl of MCCP 52 % Cl standard solution and 600 µl MCCP 57 % Cl standard solution into a 2 ml volumetric flask. 40 µl of internal standard solution is added and the flask is filled to the mark with n-Hexane.

6.2.3 Calibration solution 3 (75 µg/ml)

Transfer 600 µl of MCCP 52 % Cl standard solution and 900 µl MCCP 57 % Cl standard solution into a 2 ml volumetric flask. 40 µl of internal standard solution is added and the flask is filled to the mark with n-Hexane.

6.3 Internal Standard Solution

approx. 100 µg/ml Lindane in Hexane. Intensity of the internal standard Peak should be adjusted to TIC intensity of the middle range of the calibration curve.

7 Sampling

Material should be cut in small pieces, not larger than 3-5 mm. Adherent glue should be mechanical removed from samples as far as possible.

8 Sample preparation and analysis

8.1 Extraction of the sample

- 0,5 g ± 0,01 g test sample is weighed with the analytical balance into the sealable vessel.
- 5 ml extraction solvent (Hexane for uncoated leather, all other materials by Toluene) should be added, close Vessel tightly
- Extraction at 60 °C ± 2 °C for 60 min ± 2 min in an ultrasonic bath.
- cool down to room temperature.

8.2 Mandatory H₂SO₄-clean-up procedure

For Toluene:

- 2 ml extraction solution evaporate to dryness
- 2 ml Hexane is added, re-dissolve residue by Vortex shaking 30 sec or platform shaking (5 min/300 rpm)
- Hexane is filtrated through PTFE-membrane Filter
- 1 ml of the filtrated extract + 0,5 ml Sulfuric Acid
- shake for 10 min by Vortex or 30 min/300 rpm platform shaker
- centrifugate

- after phase separation take 0,50 ml of the hexane phase => GC-Vial
- + 10µl internal Standard solution and analyze

For n-Hexane:

- 2 ml of the extract is filtrated through PTFE-membrane Filter
- 1 ml of the filtrated extract + 0,5 ml Sulfuric Acid
- shake for 10 min by Vortex or 30 min/300 rpm platform shaker
- centrifugate
- after phase separation take 0,50 ml of the hexane phase => GC-Vial
- + 10 µl internal Standard solution and analyze

8.3 GC-MS determination

The extract is quantified using GC-NCI-MS. An example of a suitable GC-NCI-MS method is given at Annex B.

9 Calibration and Calculation

It is necessary to use at least a three point calibration.

Quantification have to be performed with internal standard correction.

Recovery of the internal standard should be >60% regarding the Area of the Internal Standard Peak of the calibration. If recovery isn't sufficient, analysis should be repeated. Recoveries lower than 60% should be noted in the Test report.

SCCP and MCCP has to be injected and calibrated separately.

Quantifier peak areas from the standards are summed up and assigned to the standard concentrations. Quantifier peak areas of the sample are summed up too and the concentration is calculated with the equation of the standard calibration, which should be in a concentration range from 1-2 x 10¹.

Note: For long sequences it will be necessary to calibrate more than one time. For checking the necessity of calibration use Calibration Check solutions

Every quantifier mass has to be within the calibration range, otherwise sample needs to be diluted.

Even if one or more chain length peaks are missing, the sample is assumed as positive for SCCP resp. MCCP.

Masses for Quantification and Qualification

CP-group	Substance	Quantifier[m/z]	Qualifier[m/z]
SCCP	C10Cl7	347	349
	C11Cl7	361	363
	C12Cl7	375	377
	C13Cl7	389	391
MCCP	C14Cl7	403	405
	C15Cl7	417	419
	C16Cl7	431	433
	C17Cl7	445	447

remarks:

C12Cl7 qualifier and quantifier ions could be switched due to interferences of m/z 375
 C17Cl7 could be critical due to interferences and low response.

10 Integration

Integration with Peak-Shape-Evaluation (PSE) Annex A

The Peak-Shape-Evaluation have been successfully tested and used.

After assessing the peak shape of the sample ion by taking the peak shape of the referring ion of the standard into account, peak is integrated in the retention time range of the standard-peak. Overlays by interfering ions are thereby avoided. Peaks with not matching peak shape are rejected and will not be integrated.

11 Disturbances

11.1 SCCP disturbances on MCCP masses

Masses used for MCCP determination can be interfered by higher concentrations of SCCP), due to interferences on the MCCP masses.

Quant mass 431 and 445 has to be quantified only if the area is above 10% of quant mass 403 or 417 and the masses are not disturbed (peak shape).

This is because of interference of SCCP ions with these masses and due to overall low response.

C11Cl7-Qualifier (m/z 363) can show a massive overload on high MCCP contents.

C12Cl7-Quantifier (m/z 375) can also show interferences on high MCCP contents

C17Cl7 Quantifier (m/z 445) shows very low response and shows overlay with SCCP-ions, therefore should be rejected upon interferences

Inlet systems have to be in clean conditions.

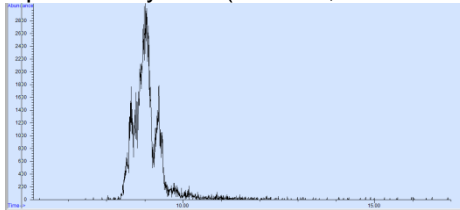
11.2 GC/ECNI-MS system optimization

System should be optimized for good Signal/Noise ratio:

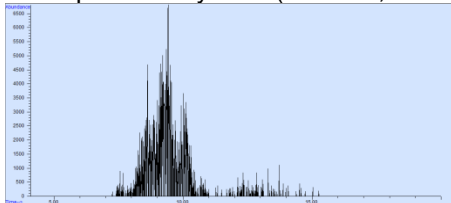
If the Scan-rate is not chosen correctly, the noisy baseline can prevent peak shape interpretation. In this case Scan rate should be changed to faster settings e.g. 2^3

Example:

Optimized system (m/z 347, Full scan mode)



Non optimized system (m/z 347, Full scan mode)



12 Test report

The test report shall include at least the following information:

- a. Reference to this test method
- b. All details necessary for complete identification of the sample tested
- c. Extraction procedure and clean-up used
- d. Any deviation by agreement or otherwise from the procedure specified
- e. Amount of detected SCCP and MCCP in mg/kg

ANNEX A Integration with peak shape evaluation (informative)

A.1 PSE (Peak-Shape-Evaluation)

- ⇒ Peaks are evaluated with reference to the corresponding peaks of the calibration standard (see Table1), regarding: Retention Time, Peak shape, Quantifier/Qualifier ratio
- ⇒ Peak-maxima-distribution and overall shape are visually evaluated.
- ⇒ Non-matching peaks should be completely rejected.
- ⇒ Partially matching peaks should be integrated only throughout the matching area (see example for m/z 347).
- ⇒ Matching peaks are integrated over their complete retention-time range. If any obvious overlays/interferences are detected, these should be excluded from integration as far as possible
- ⇒ If sample-peaks shows poor response, in a way that Peak shape-matching cannot be judged, integration over the retention-time-range of the standard peak should be done.

A.2 Quantifier/Qualifier ratio

Quantifier/Qualifier ratio should be corresponding to the ratio of the standard (a deviation of +/- 30% is be acceptable).

SCCP			
Standard	Quantifier black trace: standard 59%; blue trace: sample		
black:347 blue:349	match	partly match	no match
black:361 blue:363	match	partly match	no match
		N/A	
black:375 blue:377	375 match	375 no match	377 no match
black:389 blue:391	match	partly match	no match
		N/A	
MCCP			
Standard	black trace: standard 59%; blue trace: sample		
black:403 blue:405	match	partly match	no match
		N/A	N/A
black:417 blue:419	match	partly match	no match
		N/A	N/A
black:431 blue:433	match	partly match	no match
		N/A	N/A
black:445 blue:447	match	partly match	no match
critical, due to low response and possible massive overlay with SCCP-Ions	N/A		

ANNEX B Chromatographic parameters ref. ISO/FDIS 18219:2014 (informative)

A.1 Suggested gas chromatography mass spectrometry (GC-ECNI-MS) conditions

Column:	5 % phenyl methyl siloxane, e.g. DB-5 or equivalent is suitable length: 25 m, internal diameter: 0,25 mm film thickness: 0,25 µm
Carrier gas:	helium, flow rate: 1,2 ml/min
Injector temperature:	250 °C, mode splitless, splitless time: 1,5 min
Injection volume:	1 µl
Temperature programme:	120 °C, up to 300 °C at 12 °C/min, 300 °C for 5 min solvent delay: 4 min, total run time: 20 min
MS conditions:	Transfer line: 280 °C Ion source: 150 °C Quadrupole: 120 °C
Chemical Ionisation (CI) conditions:	CI gas: Methane 5.5 (i.e. > 99,9995 % CH ₄) CI valve: 40 %