



## **A method for the chemical modification of polychlorinated biphenyls for improved affinity towards noble metal surfaces.**

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(54) **Title:** A METHOD FOR THE CHEMICAL MODIFICATION OF POLYCHLORINATED BIPHENYLS FOR IMPROVED AFFINITY TOWARDS NOBLE METAL SURFACES

(57) **Abstract:** The present application discloses a method for the modification and analysis of a field sample suspected of containing contaminant(s) like polychlorinated biphenyls (PCBs). The invention also relates to a corresponding kit for the modification of samples suspected of containing such contaminant(s).



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A METHOD FOR THE CHEMICAL MODIFICATION OF POLYCHLORINATED BIPHENYLS FOR  
IMPROVED AFFINITY TOWARDS NOBLE METAL SURFACES

FIELD OF THE INVENTION

The present invention relates to a novel method for the modification and analysis of a field  
5 sample suspected of containing contaminant(s) having included in the structure thereof one  
or more chloro-aryl groups, such as polychlorinated biphenyls (PCBs). The invention also  
relates to a corresponding kit for the modification of samples suspected of containing such  
contaminant(s).

BACKGROUND OF THE INVENTION

10 Polychlorinated biphenyls (PCBs) are a group of organic compounds that were manufactured  
by industry back in 1926. Today it is well known that PCBs cause a number of harmful effects  
including cancer. Although this toxic group of chemicals was banned in the 1970s, they are  
still frequently found worldwide in environment, animal-source food and natural waters. PCBs  
were in particular used as an industrial chemical in constructions from the 1950'es to the late  
15 1970'es. During those years, PCBs were applied in materials like caulk, paint, glue, floor  
sealers, and double-glazed windows used by glaziers, construction workers, and other  
professionals. Due to the highly advantageous characteristics of PCBs such as longer lifetime,  
insulation and flame resistance it was a popular product in the industry.

However, PCBs eventually evaporates and poisons the indoor climate in buildings. Inhaling  
20 PCBs is damaging the human body and for this reason regulatory limits for PCBs in indoor  
climates are defined. In an international perspective, PCBs are represented as a persistent  
organic pollutant (POP) in the Stockholm Convention. In Denmark, for example, the  
challenge is to detect and effectively remove PCBs from all households. According to the  
Danish Building Research Institute, the period from the sixties to the seventies was one of  
25 the most active building periods in Denmark. Therefore, there are extremely large costs  
associated with PCB detection and subsequent removal.

Conventional PCB detection methods are usually based on gas chromatography (GC) [see,  
e.g., Zabelina et al., J. Anal. Chem. 65, 1098 (2010), and Nikonova and Gorshkov, Anal. Lett.  
44, 1290] or mass spectroscopy (MS) [Ingelido et al., Rapid Commun. Mass Spectrom. 26,  
30 236 (2012)] with reported detection limits for single PCB congeners down to 0.05-0.1 ng/L.  
Even though these methods display excellent PCB discrimination and detection capabilities,  
they require considerable effort and time.

Existing technologies attempt to directly detect PCB molecules. This has turned out to make the PCB detection extremely difficult and not practical. Therefore, several groups have realized the need to increase the affinity of PCBs towards noble metals (such as gold and silver) in connection with spectroscopic detection techniques:

5 CN 102560581 A (abstract) discloses a method for the detection of e.g. PCB-77 by means of SERS using a silver nano sheet array prepared by induced growth based on a primary cell mechanism. The reference does not indicate any chemical modification of the PCB molecule (or a PCB-containing sample) prior to the detection.

10 KR 2007-26909 A (abstract) discloses a chip for the detection of PCB molecules wherein the selectivity for PCB is improved when using the Surface Plasmon resonance detection method. The chip includes a thin gold layer on a transparent support layer and a self-assembled monolayer of an alkane compound having thiol groups at both ends (e.g. 1,3-propanedithiol, 1,4-butanedithiol, etc.). The reference does not indicate any chemical modification of the PCB molecule (or a PCB-containing sample) prior to the detection.

15 Bantz and Haynes, *Vibrational Spectroscopy* 50 (2009) 29-35, disclose the detection of PCB by SERS. The detection is improved by modification of a silver film over nanospheres (AgFON) substrate by means of an alkanethiol (e.g. decanethiol (DT)) or perfluoroalkanethiol self-assembled monolayer (SAM). PCB-47 and PCB-77 (commercial pure samples) were detected under various conditions using the modified sensor. The reference does not indicate  
20 any chemical modification of the PCB molecule (or a PCB-containing sample) prior to the detection.

Zhu et al., *J. Hazard. Mater.* (2011), 289-295, disclose the preparation of a vertically aligned silver nanoplate-assembled film for use as a sensitive SERS substrate for the detection of "analytical grade" PCB-77. The reference does not indicate any chemical modification of the  
25 PCB molecule prior to the detection thereof by SERS.

In contrast to the above, the present inventors believe that chemical modification of the PCB molecule in order to increase the affinity of PCBs towards sensor surfaces has hitherto not been suggested.

30 Bunnet and Zahler, *Chem. Rev.*, 1951, 49 (2), pp 273-412 (review), generally discloses the fundamental aromatic nucleophilic substitution reaction (replacement of an aromatic halogen by a mercaptide ion). Also, Brunelle et al., *Chemosphere*, Vol. 12, No. 2, 1983, 167-181, discloses a method for modifying PCBs by reaction with alkyl mercaptans (e.g. by using KOH

or a phase transfer catalyst) in non-polar solvents such as toluene or transformer oil so as to provide thio-ethers.

#### SUMMARY OF THE INVENTION

The present invention is based on a new approach for the detection of contaminants like, e.g., PCB using spectroscopic means (like SERS), wherein chemical modification of the contaminant molecule leads to a significant increase in the affinity of PCBs towards the noble metal surface of a sensor.

The inventors have in particular developed a method for the pre-treatment of PCB-containing field samples with the purpose of obtaining a higher sensitivity in a subsequent quantitative determination of the PCB-content by the Surface-Enhanced Raman Scattering (SERS) detection method or other applicable methods. In the pre-treatment method, a selective conversion of PCB molecules (i.e. a contaminant having included in the structure thereof one or more chloro-aryl groups) to the corresponding -S-R\* (S-H, S-alkyl, S-aryl, etc.) derivatives is obtained by an aromatic nucleophilic substitution. Such PCB-S-R\* derivatives have a relatively higher affinity for the SERS sensor surface than the native PCB molecules whereby the signal is significantly improved.

So, in a first aspect the present invention relates to a method for the modification and analysis of a field sample, cf. claim 1.

A second aspect of the invention relates to a kit for the modification of a field sample comprising contaminant(s) having included in the structure thereof one or more chloro-aryl groups, cf. claim 9, in particular contaminant(s) comprising one or more polychlorinated biphenyls (PCBs).

#### LEGENDS TO THE FIGURE

Figure 1(a) illustrates the detection of native PCB-77 on a SERS surface which results in a relatively weak SERS signal.

Figure 1(b) illustrates the detection of -S-Me modified PCB-77 on a SERS surface which results in a comparably stronger SERS signal.

## DETAILED DISCLOSURE OF THE INVENTION

As mentioned above, one aspect of the invention relates to a method for the modification and analysis of a field sample suspected of containing contaminant(s) having included in the structure thereof one or more chloro-aryl groups, e.g. polychlorinated biphenyls (PCBs).

5 *Step a) – A field sample*

Contaminants having included in the structure thereof one or more chloro-aryl groups potentially exist in a range of field samples, e.g. those which have been exposed to the respective contaminant(s) over time and which therefore may comprise traces of the contaminant(s), and those for which the production process thereof (e.g. as the case may be  
10 for certain construction materials) has included the use of contaminant(s) or precursors for contaminant(s).

In the present context, the term "field sample" is intended to encompass construction material samples, soil samples, water samples, and air samples, etc.

Field samples may be obtained simply by collecting a solid material or a liquid, by collection  
15 on a filter, or by other well-known means.

Examples of construction material samples are building material samples like concrete samples, paint samples, caulking samples, sealant samples, etc.

Construction material samples may be obtained by collecting or by cutting out a piece of the respective construction material, as the case may be.

20 Air samples may be isolated by pumping a predetermined volume of air from an enclosure through a filter whereby contaminant(s) other solid and gaseous constituents of the air can be collected on the filter.

Field samples of particular interest are those suspected of containing contaminant(s), and in particular those actually known to contain contaminant(s).

25 Contaminant(s) of interest in the present context are those which include one or more chloro-aryl groups like PCB, Insecticides, Dioxines and Dibenzofurans.

Illustrative examples of contaminants of interest are those selected from polychlorinated biphenyls (PCB), hexachlorobenzene, and pentachlorobenzene.

In one currently very interesting embodiment, the contaminant(s) is/are polychlorinated biphenyls (PCB).

5 *Step b) – Refining the field sample (optional step)*

Refining depends on the nature of the crude material. PCBs can be enriched by standard methods like Soxhlet-extraction with organic solvents like hexane. Extraction can be also done by ultrasound support with organic solvents. In many cases, grinding or powderization of the crude material is sufficient. This material is then extracted with either hexane or  
10 ethylacetate at room temperature or at reflux.

Finally, the solvent is removed by standard methods like evaporation at low pressure.

After extraction the PCBs are concentrated and some disturbing additives in crude material like polysulfides can be removed prior to treatment with alkylating agent. Polysulfides are suspected to compete with sulphur-containing contaminants with nano-surface. Oily organic  
15 compounds are suspected to coat the nano-surface.

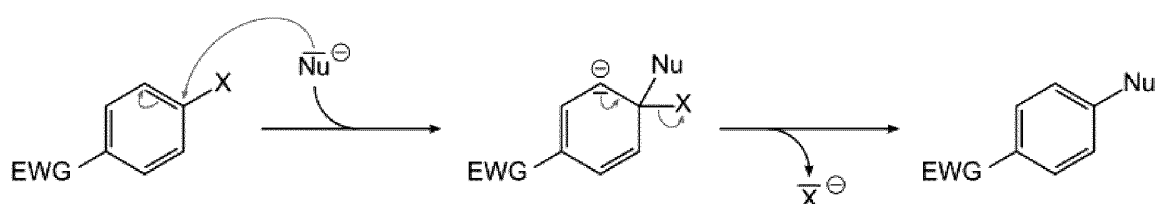
*Step c) – Treating the field sample*

In this step, the optionally refined field sample or crude powdered material is added to a high-boiling organic solvent like NMP, DMF, ethyleneglycol, glycerine, DMI, sulfolane, etc., which comprises a sulphur-introducing agent, e.g. a compound of the formula  $R^*-S^-$  counter-  
20 ion<sup>+</sup> so as to introduce  $-S-R^*$  groups in said aryl group(s) of said contaminant(s). In the  $-S-R^*$  group,  $R^*$  is typically selected from hydrogen,  $C_{1-16}$ -alkyl, and optionally substituted aryl (e.g. phenyl or naphthyl; aryl may be optionally substituted with  $C_{1-4}$ -alkyl,  $C_{1-4}$ -alkoxy, etc.), in particular from hydrogen and methyl, currently most preferred methyl. As counter-ion can act  $Li^+$ ,  $Na^+$ ,  $K^+$ ,  $Cs^+$ ,  $Rb^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ ,  $Ba^{2+}$  and organic counter-ions like  $(C_{1-4}\text{-alkyl})_4N^+$   
25 or delocalized organic cations.

By the term "high-boiling" is meant having a boiling point of at least 150 °C.

In the present context, sulphur-introducing agents are preferably those selected from alkali metal salts of alkyl-mercaptans, e.g. alkali metal salts of  $C_{1-4}$ -alkyl-SH, like  $NaSCH_3$ .

The treatment of 1 g of sample (refined field sample or crude field sample) is typically conducted with 10-100 mL of a 0.1-5 % (w/w) solution of the sulphur-introducing agent, e.g. 50 mL of 1 % (w/w) solution. This mixture is heated to elevated temperatures between 80 and 280 °C, typically to 200 °C, for 5 min to 5 h, typically 20-30 minutes. By the reaction  
 5 between the sulphur-introducing agent and the chloro-aryl group(s) of the contaminant(s), a modified sample is obtained.



X = chlorine, Nu = R<sup>\*</sup>-S<sup>-</sup>, EWG = electron withdrawing group (in case of PCB a second chlorine)

10 In some preferred embodiments, the sulphur-introducing agent is NaSCH<sub>3</sub>. The contaminant(s) have one or more chloro-aryl groups, e.g. like PCB, whereby a -S-Me groups can replace one or more chlorine atoms but at least one by an aromatic nucleophilic substitution reaction.

*Step d) – Purifying the modified sample (optional step)*

15 The reaction mixture is typically poured into water and extracted with an organic solvent like ethyl acetate. Optionally, the organic layer can act as a filter to remove insoluble substances. After the removal of all volatiles the modified sample is obtained.

*Step e) – Contacting the modified sample with a sensor surface*

20 This step involves the contacting of the modified, optionally purified sample with a noble metal surface of a sensor, e.g. a surface-enhanced Raman scattering (SERS) sensor.

In the present context, the term "noble metal" is intended to mean one or more of ruthenium, rhodium, palladium, silver, osmium, iridium, platinum and gold. Particularly useful examples of noble metals are gold, silver and platinum.



Due to high affinity of sulphur in oxidation status II to noble and transition metals a nearly covalent bond between sulphur and metal is formed responsible for immobilisation and absorption of the modified samples on the surface.

In some embodiments, the noble metal sensor surface is a nanostructured noble metal (e.g. gold or silver) surface that qualifies as a SERS substrate (e.g. nanopillars, nanotubes, colloidal nanoparticles, any nanosized object capable to confine the incident radiation and create the so-called "hot spots"), in particular a noble metal surface of a SERS sensor. Preparation of nanostructured surfaces of sensors is e.g. described in: Meikun Fan, Gustavo F.S. Andrade, Alexandre G. Brolo, A review on the fabrication of substrates for surface enhanced Raman spectroscopy and their applications in analytical chemistry, *Analytica Chimica Acta*, Volume 693, Issues 1–2, 5 May 2011, Pages 7-25; Bhavya Sharma, Renee R. Frontiera, Anne-Isabelle Henry, Emilie Ringe, Richard P. Van Duyne, SERS: Materials, applications, and the future, *Materials Today*, Volume 15, Issues 1–2, January–February 2012, Pages 16-25; J. Hübner, and A. Boisen, *Adv. Mater.* **24**, 11 (2012); and [Ralph A. Tripp, Richard A. Dluhy, Yiping Zhao, Novel nanostructures for SERS biosensing, *Nano Today*, Volume 3, Issues 3–4, June–August 2008, Pages 31-37].

*Step f) – Detecting the presence of contaminant(s)*

The final step includes the detection of the presence of the contaminant(s) in the modified sample by spectroscopic means, e.g. spectroscopic means selected from Raman spectroscopy, such as surface-enhanced Raman spectroscopy (SERS), quartz crystal microbalance (QCM) and surface plasmon related biosensing/detection techniques.

In one interesting embodiment the spectroscopic means is surface-enhanced Raman spectroscopy (SERS).

The abbreviation "SERS" refers to the interchangeable terms "Surface-Enhanced Raman Spectroscopy" and "Surface-Enhanced Raman Scattering".

The SERS detection is performed using a Raman scattering spectrometer equipped with an excitation laser or a home/lab build setup that delivers the same function, and a nanostructured (e.g. nanopillars, nanocubes) SERS surface. Modified PCB containing liquid or gas can then be deposited on the nanostructured surface by e.g. droplet deposition, immersion, exposure to gas, evaporation, etc. Further steps can be introduced to increase the SERS signal from PCB molecules or promote the affinity of PCBs towards the SERS

substrate, e.g. deposition of additional liquids or solvents, employing magnetic fields, pressure or flow. The SERS signal is then collected using a Raman scattering spectrometer.

In one embodiment, the detection in step f) also includes the quantitative determination of the contaminant(s) in the modified sample.

- 5 Modified PCB molecules display affinity towards the SERS substrate. The measured SERS signal intensity is proportional to the number of modified PCB molecules on/close to the SERS substrate. By employing an identical SERS signal collection conditions, the recorded SERS intensity gradually decreases as the concentration of modified PCB molecules is decreased. The relationship can then be used as a calibration curve to estimate unknown concentrations  
10 of the modified PCB molecules.

#### *A kit*

- A second aspect of the invention relates to a kit for the modification of a field sample, said kit comprising a container holding a 0.1-5 %(w/w) solution of an sulphur-introducing agent (e.g. an alkali metal salt of a C<sub>1-4</sub>-alkylmercaptan) in a high-boiling solvent (e.g. NMP, DMF,  
15 ethylene glycol, glycerine, DMI, sulfolane, etc.). The kit preferably further comprises a separating device (e.g. a separating funnel), and/or a filtering device. The separating device and/or the filtering device may if desired be incorporated in the container holding the solution of the sulphur-introducing agent. Also, the kit may comprise a heating unit (e.g. an electrical heating device or a microwave heating device).
- 20 The kit is particularly useful for the modification of a field sample comprising one or more contaminant(s) having included in the structure thereof one or more chloro-aryl groups, in particular contaminants comprising one or more polychlorinated biphenyls (PCBs). In particular, the kit is useful in the method described hereinabove.

#### EXAMPLES

- 25 *Synthesis of -SCH<sub>3</sub> modified PCB-77*

Modified PCB-77 molecules were synthesized in four steps: (a) 200 ml of sulfuric acid was cooled down to -20 °C followed by addition of powdered sodium nitrite (32 g = 463 mM). The mixture was allowed to warm up to 55 °C and was cooled down to 0°C. 3,4-Dichloroaniline (50 g = 30 mM) was added and stirred for additional 30 min at this temperature and then 1h

at room temperature. The diazonium solution was dropped to a solution of potassium iodide (154 g = 926 mM) in 500 g of ice and 200 mL of water. After 30 min sodium bisulfite was added to colourless mixture and extracted 3x with chloroform. After drying, the solvent was removed and the residue distilled at 0.1 Torr to give at bp. 85-90°C, 67g = 80 % yield of the  
5 desired compound as orange oil. (b) A solution of 3,4-dichloro-iodobenzene (33.5 g = 123 mM) in 250 mL of THF was cooled down to -80°C followed by addition of 54 mL n-BuLi in hexane (2.5 g = 135 mM). After 25 min at this temperature copper dibromide (28 g = 125 mmol) was added in small portions. After 3h at -80°C this solution was given on saturated ammonium chloride in water. The product was filtered and water was extracted with  
10 chloroform to give additional amounts of product. Recrystallization from hexane gave 17.3 g = 96 % yield of slightly yellow crystals with mp. 176°C. (c) A mixture of 7.18 g (246 mM) 3,3,4,4-tetrachlorobiphenyl and 1.9 g (271 mM) MeSNa in 75 mL sulfolane was heated up to 110°C for 18 h under N<sub>2</sub> atmosphere. After cooling down, the mixture was poured into 1 L of water and filtrated to obtain 7 g of a white crystalline powder. All synthesis products in steps  
15 (a)-(c) were verified using NMR measurements.

#### *SERS substrate fabrication and detection principle*

Gold metal coated silicon nanopillars were fabricated following the protocol described in M. S. Schmidt, J. Hübner, and A. Boisen, Adv. Mater. **24**, 11 (2012). The SERS substrate is produced using mask-less lithography and involve two fabrication steps. First, silicon  
20 nanopillars were produced using SF<sub>6</sub> and O<sub>2</sub> reactive ion etching process. After the silicon etching cycle, the surface was further treated with Ar and O<sub>2</sub> plasmas to remove fluorine and sulphur related products. Second, 200 nm thick gold film was deposited using electron beam evaporation and the surface exhibited dark red colour. Inspection in a scanning electron microscope showed that the SERS substrate consisted of ≈500 nm in height gold-capped  
25 nanopillars that are roughly perpendicular to the silicon surface. The gold cap is approximately ellipsoidal with average dimensions a≈300 nm and b≈100 nm in height and width, respectively.

#### *Raman and SERS spectroscopy*

Raman and SERS measurements were performed using Thermo Scientific DXR Raman  
30 Microscope. An optical microscope is coupled to a single grating spectrometer that delivers 5.0 cm<sup>-1</sup> FWHM spectral resolution and ±2.0 wavenumber accuracy. Frequency-stabilized single mode diode laser operated at 780±0.2 nm. All solid-state Raman and SERS spectra were recorded using 10x long working distance objective and laser powers of 5 and 0.1 mW, respectively. Signal collection time was set to 5 seconds, unless stated otherwise. To ensure

that there are no observable spectral changes associated with thermal or photo-induced processes, series of SERS spectra were monitored for prolonged periods of time (minutes). Solid-state Raman spectra were recorded from small crystals (10-50  $\mu\text{m}$ ) deposited on a glass slide. Both PCB-77 and PCB-77-SCH<sub>3</sub> compounds were dissolved in isopropanol (IPA, C<sub>3</sub>H<sub>8</sub>O) using magnetic stirring (12 h) and concentrations ranged from  $5 \cdot 10^{-3}$  down to  $5 \cdot 10^{-8}$ . The SERS substrates were then immersed in PCB solutions of varying concentrations for 3 h, rinsed thoroughly with IPA (not PCB-77) and left for drying to form micro-sized clusters. In addition, PCB-77 molecules were also dissolved in THF and the recorded SERS spectra were identical to the ones produced using isopropanol.

## 10 *Numerical calculations*

All numerical calculations were performed using the program package Gaussian 09 [Frisch et al., Gaussian 09 Revision A.1, Gaussian Inc. Wallingford CT 200935]. The vibrational frequencies, IR and Raman intensities were obtained numerically. The ground-state molecular structures were optimized utilizing density functional theory (DFT) calculations using the hybrid functional B3LYP [Svedberg et al., J. Phys. Chem. B **110**, 25671 (2006), Becke, J. Chem. Phys. **98**, 5648 (1993), and Alaverdyan et al., Phys. Chem. Chem. Phys. **8**, 1445 (2006).] and the standard 6-31G\*basis set. In order to correct for systematic errors, all computed frequencies were scaled by a factor according to Scott and Radom, J. Phys. Chem. **100**, 16502 (1996).

## 20 *Results and Discussion*

In Figure 1(a)-(b) the SERS detection principle utilizing gold-capped silicon nanopillars for standard and modified PCB-77 is schematically illustrated. In the PCB-77 case, the metal-molecule link is not expected to occur, and therefore micro clusters of nanopillars encapsulate few random PCB-77 molecules. The SERS measurements using different concentrations of PCB-77 ranging from  $5 \cdot 10^{-3}$  to  $5 \cdot 10^{-6}$ M are show in Figure 2. The Raman spectral characteristics diminish and are essentially not visible at below monolayer coverage. Due to low solubility of PCB-77 in isopropanol, we have verified the result using a moderately polar THF solvent [K. C. Bantz and C. L. Haynes, Vibrational Spectroscopy **50**, 29 (2009)]. SERS spectra of PCB-77 using THF were similar to the result in Figure 2, hence the solid state and SERS spectral differences cannot be related to solvent effects.

For the modified PCB-77 case, the metal-molecule interaction is expected to improve the SERS signal because molecules are effectively concentrated within the high electromagnetic field area, see Figure 1(b). The SERS spectra of PCB-77-SCH<sub>3</sub> with concentrations varying

from  $5 \cdot 10^{-3}$  to  $5 \cdot 10^{-8}$  M are presented in Figure 3 and are very similar to the solid state vibrational pattern. Chemical stability of the modified PCB-77 molecule on the gold surface was verified by recording the SERS signal for prolonged periods of time (minutes). No significant signs of transient effects similar to the ones observed for 2,2':5',2''-terthiophene  
5 in ref. [Y. Alaverdyan, P. Johansson, and M. Kall, Phys. Chem. Chem. Phys. **8**, 1445 (2006)] were identified. We therefore interpret our result as a consequence of metal-molecule link via sulfur atom that inhibits any photo-induced structural changes of the modified PCB molecule. Contrary to the PCB-77 case, the entire molecular fingerprint of PCB-77-SCH<sub>3</sub> is preserved down to the nanomole regime.

## CLAIMS

1. A method for the modification and analysis of a field sample, said method comprising:
  - a. obtaining a field sample containing contaminant(s) having included in the structure thereof one or more chloro-aryl groups;
  - 5 b. optionally refining said field sample;
  - c. treating said optionally refined field sample with a sulphur-introducing agent so as to introduce -S-R\* groups in said chloro-aryl group(s) of said contaminant(s), R\* being selected from hydrogen, C<sub>1-16</sub>-alkyl, and optionally substituted aryl, thereby obtaining a modified sample;
  - 10 d. optionally purifying said modified sample;
  - e. contacting said modified, optionally purified, sample with a noble metal surface of a sensor;
  - f. detecting the presence of said contaminant(s) in said modified sample by spectroscopic means.
- 15 2. The method according claim 1, wherein the sulphur-introducing agent is an alkali metal salt of a C<sub>1-4</sub>-alkylmercaptan
3. The method according claim 2, wherein the sulphur-introducing agent is NaSCH<sub>3</sub>.
4. The method according to any one of the preceding claims, wherein contaminant(s) is/are polychlorinated biphenyls (PCB).
- 20 5. The method according to any one of the preceding claims, wherein the spectroscopic means is selected from Raman spectroscopy, such as surface-enhanced Raman spectroscopy (SERS), quartz crystal microbalance (QCM), X-ray photoelectron spectroscopy (XPS) and surface plasmon related biosensing/detection techniques.
6. The method according to any one of the preceding claims, wherein in step (e) the  
25 sensor is a surface-enhanced Raman scattering (SERS) sensor.

7. The method according to any one of the preceding claims, wherein in step (c) the sample is treated with 10-100 mL of a 0.1-5 % (w/w) solution of the sulphur-introducing agent per gram of sample, and is heated to a temperature in the range of 80-280 °C for 5 min to 5 h.
- 5 8. The method according to any one of the preceding claims, wherein the detection in step (f) includes the quantitative determination of said contaminant(s) in said modified sample.
9. A kit for the modification of a field sample comprising contaminant(s) having included in the structure thereof one or more chloro-aryl groups, said kit comprising a container  
10 holding a 0.1-5 % (w/w) solution of an sulphur-introducing agent in a solvent having a boiling point of at least 150 °C, and further comprises a separating device and/or a filtering device.
10. The kit according to claim 9, wherein the separating device and/or the filtering device is incorporated in the container holding the solution of the sulphur-introducing agent.
11. The kit according to any one of the claims 9-10, wherein the contaminant(s) include  
15 one or more polychlorinated biphenyls (PCBs).
12. The kit according to any one of the claims 9-11 for use in the method according to any one of the claims 1-8.

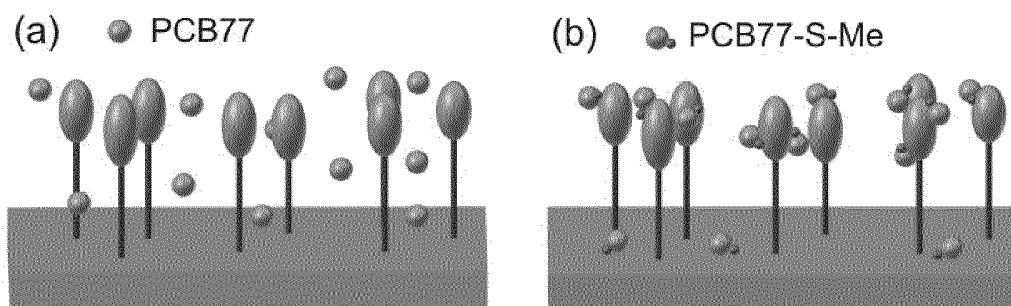


Fig. 1



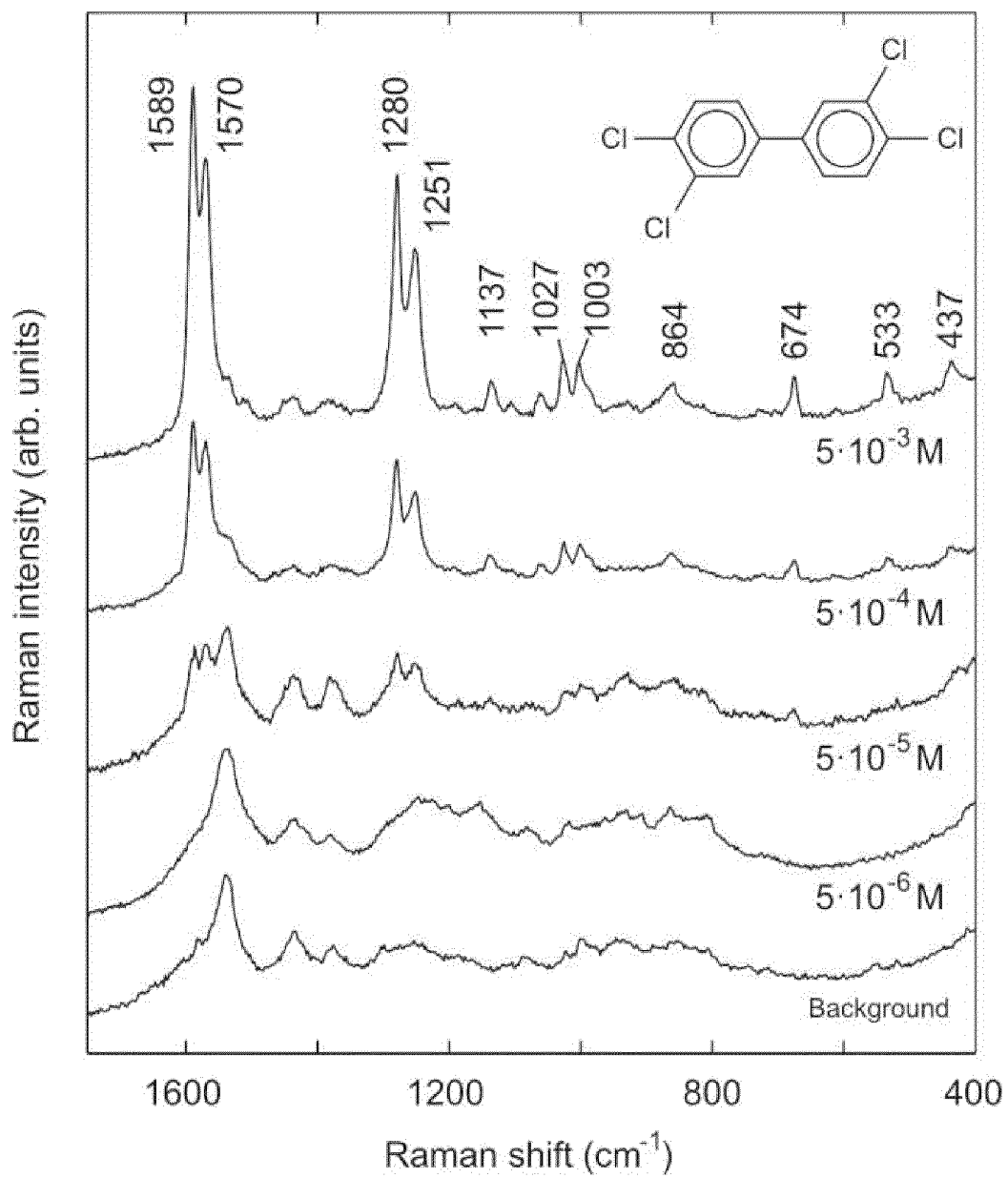


Fig. 2

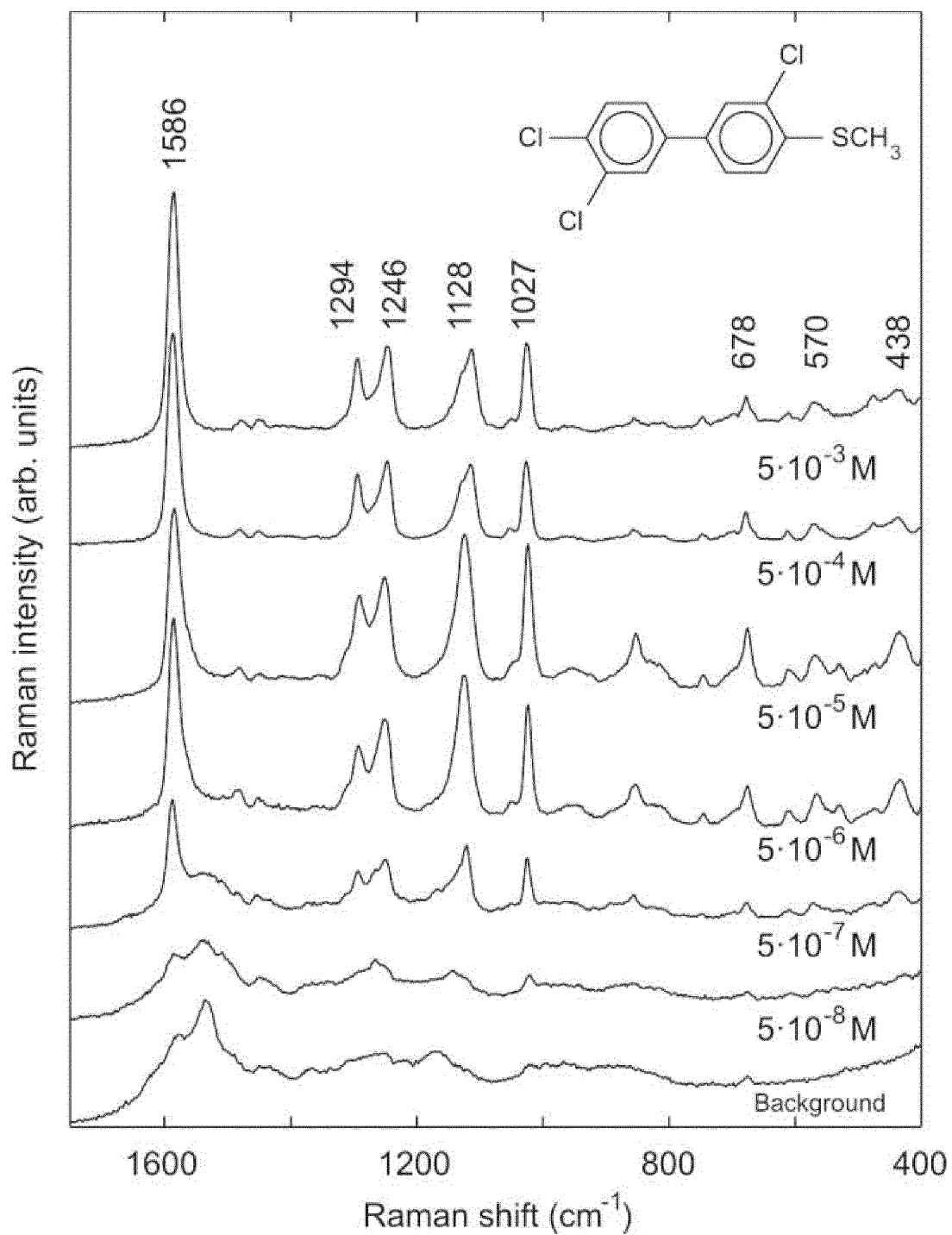


Fig. 3

# INTERNATIONAL SEARCH REPORT

International application No PCT/EP2015/062925
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<b>A. CLASSIFICATION OF SUBJECT MATTER</b> INV. G01N33/24      G01N33/00 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols) G01N		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data, BIOSIS, EMBASE, FSTA, INSPEC, MEDLINE		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	D.J. BRUNELLE: "Reaction of polychlorinated biphenyls with mercaptans in non-polar media: Formation of polychlorobiphenyl sulfides", CHEMOSPHERE, vol. 12, no. 2, 1 January 1983 (1983-01-01), pages 167-181, XP055152444, ISSN: 0045-6535, DOI: 10.1016/0045-6535(83)90160-1	1-3,5-9
Y	page 168	10-12
A	page 170	4
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <span style="margin-left: 100px;"><input checked="" type="checkbox"/> See patent family annex.</span>		
* Special categories of cited documents :		
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family	
"P" document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search	Date of mailing of the international search report	
6 August 2015	17/08/2015	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  Michalitsch, Richard	

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## INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2015/062925

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	BANTZ K C ET AL: "Surface-enhanced Raman scattering detection and discrimination of polychlorinated biphenyls", VIBRATIONAL SPECTROSCOPY, ELSEVIER SCIENCE, AMSTERDAM, NL, vol. 50, no. 1, 26 May 2009 (2009-05-26), pages 29-35, XP026089901, ISSN: 0924-2031, DOI: 10.1016/J.VIBSPEC.2008.07.006 [retrieved on 2008-07-23]	1-3,5-9
Y A	Experimental Section points 3.1-3.3 -----	10-12 4
X	EP 2 354 146 A1 (NAT UNIV KANGNUNG WONJU IND AC [KR]) 10 August 2011 (2011-08-10)	1-3,5-9
Y A	paragraphs [0014], [0015] example 1 example 56 -----	10-12 4
A	KR 2007 0026909 A (SEOUL NAT UNIV IND FOUNDATION [KR]) 9 March 2007 (2007-03-09) cited in the application the whole document -----	1-12

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2015/062925

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
EP 2354146	A1	10-08-2011	CN 102307885 A	04-01-2012
			EP 2354146 A1	10-08-2011
			JP 2012505076 A	01-03-2012
			KR 20100041565 A	22-04-2010
			US 2011223318 A1	15-09-2011
			WO 2010044523 A1	22-04-2010
-----				
KR 20070026909	A	09-03-2007	NONE	
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