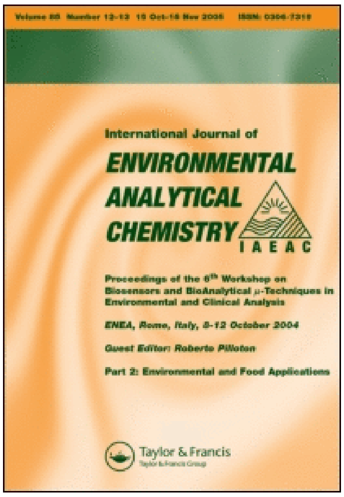

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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Bernhard Wehling[a]; Wieland Hill[a]; Dieter Klockow[a]
[a] Institut für Spektrochemie und Angewandte Spektroskopie (ISAS), Dortmund, Germany

To cite this Article Wehling, Bernhard , Hill, Wieland and Klockow, Dieter(1999) 'Detection of Aromatics in the Gas Phase by Surface-Enhanced Raman Scattering on Substrates Chemically Modified with *p-tert*-Butylcalix[4] Arenetetrathiol', International Journal of Environmental Analytical Chemistry, 73: 3, 223 — 236

To link to this Article: DOI: 10.1080/03067319908032665

URL: http://dx.doi.org/10.1080/03067319908032665

Intern. J. Environ. Anal. Chem., Vol. 73(3), pp. 223-236
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DETECTION OF AROMATICS IN THE GAS PHASE BY SURFACE- ENHANCED RAMAN SCATTERING ON SUBSTRATES CHEMICALLY MODIFIED WITH *p-tert*-BUTYLCALIX[4] ARENETETRATHIOL

BERNHARD WEHLING, WIELAND HILL* and DIETER KLOCKOW

Institut für Spektrochemie und Angewandte Spektroskopie (ISAS) PO Box 101352, D-44013 Dortmund, Germany

(Received 15 July, 1998; In final form 28 December, 1998)

In this paper the possibilities are demonstrated to detect gaseous aromatic compounds by surface-enhanced Raman scattering (SERS) on substrates chemically modified with *p-tert*-butylcalix[4]arenetetrathiol (BCAT). Benzene, toluene, ethylbenzene, and isomers of xylene are reversibly deposited through interaction with the surface-bound BCAT molecules. Due to this interaction, the detection limits for the investigated aromatics are decreased in comparison to mere adsorption at bare metal surfaces. The limits of detection were found to be between 1.2 and 3.1 mg/L for all substances. The dynamic range for the detection of gas phase concentrations is up to two orders of magnitude with a roughly linear relationship between SERS band intensities and concentrations. The response time of the SERS sensor is about one minute.

Keywords: Surface-enhanced Raman scattering; gaseous aromatic compounds; chemical modification; calixarene

INTRODUCTION

Surface-enhanced Raman scattering (SERS) at rough metal films or particles can be used to detect and characterize submonomolecular layers of adsorbed organic substances. Therefore, SERS is a promising method for chemo-optical sensing of organic trace compounds in environmental media. The application of SERS in sensors has, however, been limited by unfavourable properties of the widely used bare metal surfaces: instability due to its chemical reactivity, contamination by adsorption of unwanted substances in competition with the desired analytes.

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* Corresponding author. Fax: +49–231–1392120, E-mail: hill@isas-dortmund.de.

Organic coating of metal SERS substrates proved to be useful to improve stability and adsorption properties significantly[1]. Stable, ultrathin and homogeneous coatings at metals can he generated by chemical reaction with thio-organics[2].

Complexing reagents can interact reversibly and stoichiometrically with other organic or inorganic components. If such reagents are fixed to sensor surfaces, the ratio of coating and analyte signals should be determined by thermodynamic equilibria. The use of signals of complexing coatings as internal standards should therefore improve quantification of analytes in comparison with adsorption at bare metal surfaces or surfaces hydrophobized with alkane derivatives. Complexation at SERS substrate surfaces was demonstrated for alkali metal ions with immobilised thiol-derivatized dibenzo-18-crown-6[3] and for methyl orange with thiol-derivatized cyclodextrin[4].

In a preceding work[5], aromatics in water were detected by complexation at SERS substrates chemically modified with BCAT in the same way as in the present paper. The complexation with BCAT was completely reversible and lowered the detection limits considerably in comparison with bare metal substrates.

Vo-Dinh et al. demonstrated that uncoated SERS substrates can be used as passive monitors for the dosimetry of vapours of benzoic acid and terephthaldehyde in low concentrations[6]. Authors of the same group showed that saturated vapours of two nerve agent simulants can also be detected by SERS[7]. Carron et al. detected concentrated vapours of benzene, toluene, isomers of xylene and ethylbenzene by SERS at propanethiol coated substrates with fast response[8, 9]. However, there still exists only limited knowledge on the range of detectable substances and concentrations in the gas phase in comparison to the broadly investigated field of SERS in solutions.

Benzene, toluene, isomers of xylene and ethylbenzene (BTXE) are aromatics with six to eight carbon atoms that are ubiquitously distributed in the environment due to their release by industrial processes and automobiles. Concentrations of BTXE in work place or ambient air or in waste gases need to be monitored because of the carcinogenic potential of benzene and the toxic action of the other substances on the central nerve system. In the present paper, the analysis of BTXE by SERS at BCAT coated substrates is reported as a new method for the fast detection of these substances in the gas phase.

EXPERIMENTAL SECTION

Raman spectroscopy

Raman measurements were carried out with a DILOR XY triple monochromator with subtracting dispersion of the first two stages. A cw Ti:sapphire laser (Coherent 890) operating at a wavelength of 702 nm served as the excitation source. The laser radiation was filtered by a grating monochromator for removal of spontaneous emission background. A Wright Instruments nitrogen cooled CCD camera with a 298 × 1152 pixel EEV 88131 chip served as detector. The Raman spectra were measured in back-scattering geometry using f/1.0 collection optics. To prevent heating of the surface, which might cause desorption of analyte or degradation of SERS substrates, a cylinder lens with f = 200 mm was used to generate a line focus at the substrate.

Substrate preparation

Segments of glass slides for microscopy with a thickness of 1 mm were purified by immersion in hot HNO_3 for two hours, followed by rinsing with high-purity water and drying. Then the slides were spin-coated at 2000 rpm with 150 µL of a 5 % aqueous suspension of alumina particles with a nominal size of 0.3 µm[10]. After drying again, the substrates were coated with 2 nm of chromium and 75 nm of 99.99% silver by evaporation and deposition in vacuum. The chromium layer served for an improved adhesion between silver and the glass substrate.

Silver surfaces were coated with BCAT by immersion of the slides into a 0.1 mM toluenic solution for two hours. SERS spectra of BCAT coatings were reported earlier[5]. Complete disappearance of S-H stretching bands after bonding to the surface indicated the formation of four S-Ag bonds for at least the major part of the molecules.

After coating with BCAT, the substrates were rinsed with pure toluene, dried, and then immersed into a 10 mM NaCl solution for 5 minutes, such increasing the SERS-intensities by approximately 50%. Such additional "chemical" enhancements of SERS by the action of anions have been utilised for years, although the mechanism behind is not completely understood yet[11]. After rinsing with water and drying the slides were ready for use.

Chemicals

Benzene (p.a., > 99.7% GC), toluene (uvasol, > 99.9% GC), and *m*-xylene (extrapure, > 99% GC) were obtained from Merck. Ethylbenzene (puriss. p.a., > 99% GC), *p*-xylene (puriss. p.a., > 99% GC), and *o*-xylene (puriss. p.a., > 99% GC) were obtained from Fluka and used as delivered. High purity water with an electrical conductivity below 0.07 µ S/cm was produced by a commercial water purification system (Millipore Milli-Q) equipped with an additional filter for organics. BCAT was prepared from p-tert-butylcalix[4]arene by Gibbs and Gutsche according to their method described elsewhere[12].

Preparation of test gas mixtures

The apparatus schematically shown in Figure 1 was used for test gas generation and flow control. Gaseous nitrogen with 99.999 % purity was produced by evaporation of liquid nitrogen. After pressure reduction, traces of water and organic impurities were removed by molecular sieve and activated carbon filters. Then the gas stream passed a flow controller operating down to flow rates of 1 mL/min. A 4-port valve (Valco C4WP) allowed to send the gas either directly to the measuring cell (Fig. 2) or through a glass flask for evaporation of analytes. The 280 mL evaporation flask was equipped with a septum for the injection of liquid analytes and contained a glass coated magnetic stirrer for continuous mixing of the gas. A soap bubble flowmeter was used to measure flow rates downstream the measuring cell. Gas lines between valve, flask and cell had an overall length of 10 cm and an inner diameter of 1 mm.

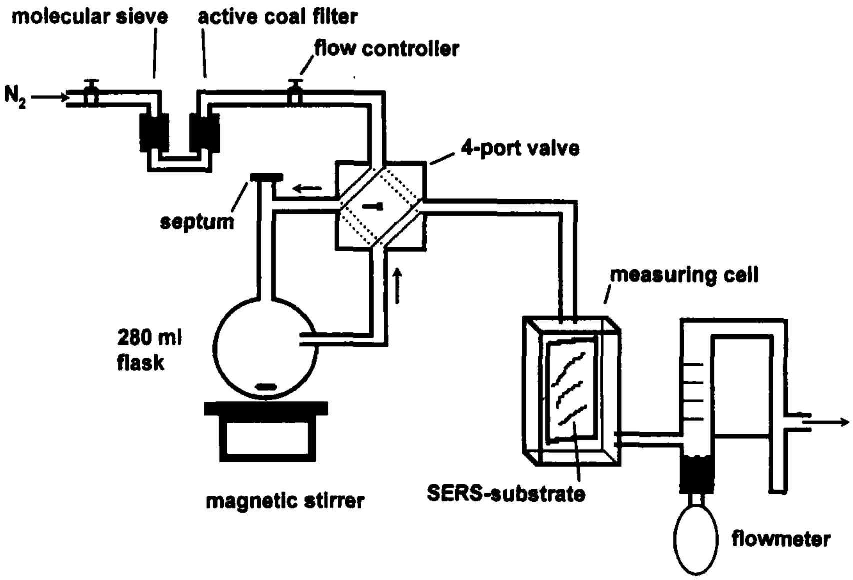

FIGURE 1 Scheme of the test gas generation and measuring cell

Evaporation of 1 μL of the respective liquid analyte within the 280 mL flask resulted in gas concentrations of about 3.1 mg/L assuming complete evaporation of the liquids and uniform mixing of the vapours with the carrier gas.

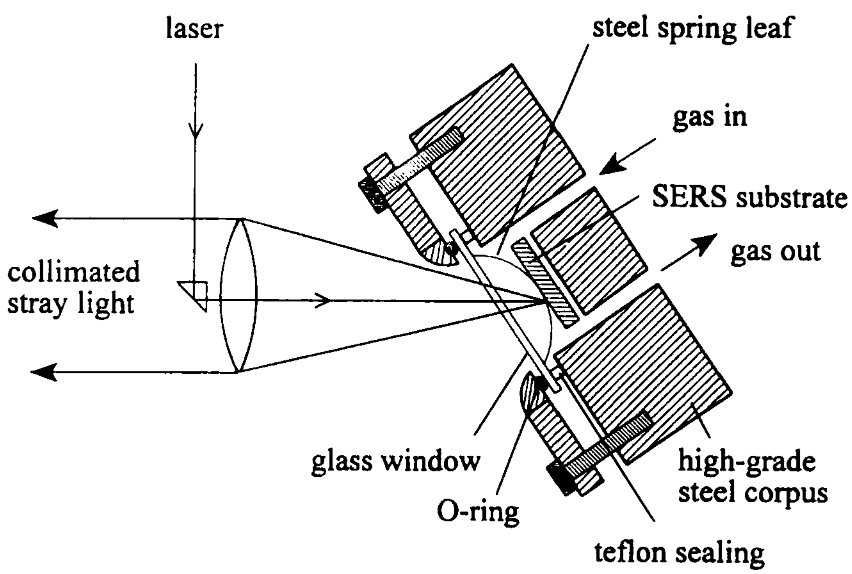

FIGURE 2 Cross sectional view of the measuring cell. The cell had a gas volume of about 0.2 mL and a diameter of the window of 25 mm. Window, gas layer and SERS substrate had thicknesses of 1 mm each. The Teflon® sealing was only 0.2 mm thick, by which memory effects were minimised. Gas in- and outlet were made using 1/16″ Swagelok® connectors

SERS measurements of concentration dependencies

The first spectrum of each substrate was taken under pure nitrogen before adding any analyte. Then an analyte was injected into the evaporation flask. Two minutes after complete evaporation of the liquid the valve directing the gas flow through the evaporation flask was opened. Further 5 minutes were waited before starting the second SERS measurement to avoid possible influences of concentration gradients built up within the measuring cell and to allow adsorption to reach the equilibrium. Standard signal integration lasted 4 min. Integration times of 10 min were used for weak signals to improve the signal to noise ratio.

The flow was always held constant at 1 mL/min. It took a comparatively long time to dilute the gas in the evaporation flask significantly at this small flow rate. The calculated final concentration in the evaporation flask after the maximum time of 15 min was about 95% of the initial value.

SERS measurements as a function of time

Spectra were taken every minute for the investigation of the temporal behaviour of adsorption. After five measurements under nitrogen, the respective analyte was applied two times for periods of 10 minutes with intermediate flushing with nitrogen for 10 minutes. Ten further spectra were taken under nitrogen after the second application of analyte.

A photo ionisation detector (PID) was placed downstream the measuring cell to control the development of the gas concentration. A few seconds after opening the evaporation flask, the analyte reached the detector leading to about 80% of the final signal within 2 s and developing the full signal within 5 to 10 s. This delay can be neglected considering the integration time of SERS measurements of 1 min. The decrease of analyte concentrations was also controlled by the PID. The decay was similarly fast as the increase and no noticeable desorption from cell materials could be observed. It should be mentioned, however, that worse results were obtained using a cell made essentially of Teflon®.

RESULTS AND DISCUSSION

Comparison of coated and uncoated substrates

BCAT coated substrates adsorb all BTXE aromatics as described in detail below. Adsorption of the analytes can also be observed at uncoated substrates at high gas concentrations. The intensities of the analyte bands are, however, three to five times larger for coated substrates in comparison to uncoated ones at the same concentration.

The SERS enhancement decreases strongly with increasing distance of a certain species from the metal surface. Therefore, the SERS intensity from an analyte molecule within a BCAT cage should be smaller than from the same molecule adsorbed directly at the bare metal surface. In addition, the number of adsorption places within the bulky BCAT cages should be clearly smaller than that at a bare metal surface. However, the SERS intensities are stronger at the chemically modified surfaces pointing to a greater affinity of analyte molecules to the BCAT cage than to the metal surface.

After exposure to air and even after storage under pure nitrogen, uncoated substrates exhibit several SERS bands indicating adsorption of organic molecules. These impurities cannot be removed by flushing with high-purity nitrogen, and they make adsorption of the investigated analytes irreproducible. Impurity bands are strongly reduced by coating with BCAT, and reproducible adsorption of analytes can be achieved at coated substrates.

A further advantage of the BCAT coated substrates is that the BCAT SERS bands, e.g. that at 1037 cm^{-1}, can serve as an internal standard in the measurement of analytes. By this means, SERS band intensities can be used as a measure for the surface concentration of analytes that is independent of the actual SERS enhancement of the respective substrate and the experimental conditions applied. In the present investigation, the absolute band intensities of adsorbed analytes varied by factors up to three for measurements at different substrates under the same analyte concentration. Calibration of analyte bands in relation to the BCAT band at 1037 cm^{-1} improved the reproducibility clearly and resulted in relative standard deviations of typically 10 %.

Adsorption at bare metal or thioalkane coated surfaces can depend on collective phenomena such as interactions of adsorbed species or ordering processes in the coating layer. Therefore, the adsorption may exhibit complicated isotherms or depend on the quality of the coating. However, a reversible stoichiometric adsorption through inclusion complexation with immobilised BCAT is mainly determined by the structure of the involved molecules and by thermodynamic equilibria.

SERS spectra

All six investigated substances were adsorbed at the BCAT modified surfaces: benzene, toluene, ethylbenzene and the isomers of xylene. If an analyte is adsorbed at the BCAT-coated silver surface, the SERS-spectrum apparently is a pure superposition of the SERS-spectrum of the BCAT coated substrate and the Raman spectrum of the pure substance as it was already observed for adsorption of aromatics from aqueous solutions[5]. No changes of the band positions of the pure substance due to its interaction with the surface were noticed.

The positions of the strongest bands are clearly influenced by the substituents at the aromatic ring. Therefore, the adsorbed aromatic species can be identified by their SERS spectra if their surface concentrations are large enough to measure at least one or two of these bands.

SERS signals as a function of concentration

Measurements at varying concentrations were made considering the heights of the following strong bands: 992 cm^{-1} for benzene (Fig. 3), 1002 cm^{-1} for toluene, 1003 cm^{-1} for ethylbenzene, 734 cm^{-1} for *o*-xylene, 725 cm^{-1} for *m*-xylene and 825 cm^{-1} for *p*-xylene. The intensity of the BCAT band at 1037 cm^{-1} was used as internal standard to normalise the band intensities of the aromatics as shown in Figure 3 with the example of benzene.

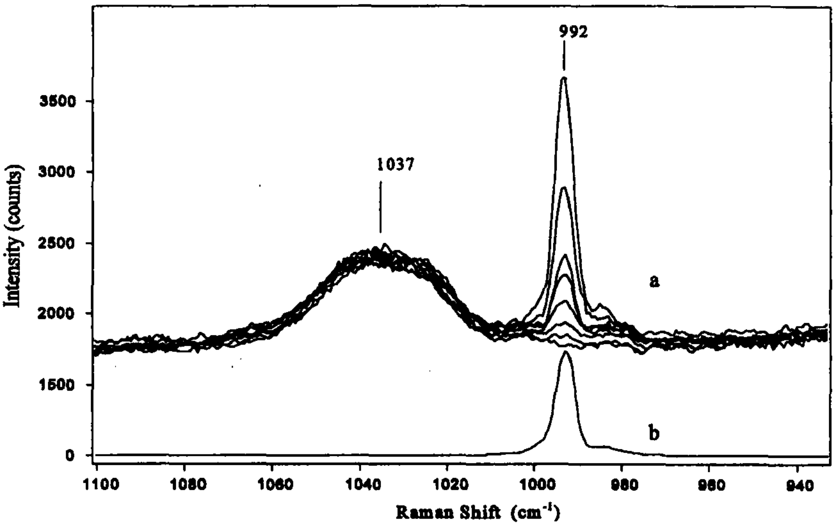

FIGURE 3 SERS spectra of BCAT substrates with adsorbed benzene at different gas phase concentrations (a). The band height at 992 cm^{-1} increases with the concentration of benzene, which was 0, 3.14, 6.28, 12.56, 31.4, 62.8, 125.6 or 314 mg/L, respectively. The broad band at 1037 cm^{-1} is due to the BCAT-coating. It was used for normalisation of the spectra. The Raman spectrum of liquid benzene is given for comparison (b)

Figures 4 and 5 show the normalised results in double logarithmic plots. Concentration ranges of one to two orders of magnitude could be covered for each of the substances. The ranges were limited at the high end by the vapour pressure of the analytes and at the low end by the noise of the broadband background signal from the SERS-substrates. The concentration curves fit reasonably well to linear functions without indications for saturation of the surfaces at higher concentrations. Therefore, it can be assumed that full sorption capacity was not reached even at the high gas concentrations close to the vapour pressures.

The limits of detection were found for all substances to be between 1.2 and 3.1 mg/L. These comparatively high limits as well as missing saturation of surfaces at high concentrations point to a rather weak affinity of the analyte molecules to the immobilised BCAT cages. Further lowering of detection limits would require the immobilisation of centres exhibiting stronger interactions with the analytes than the mere van der Waals interaction with BCAT[5].

The slope of the calibration curves is smaller than unity, different from what is expected for Langmuir adsorption, and slightly dependent on the adsorbed substance as it was already observed for adsorption from aqueous solutions[5]. Possibly, the relative band intensities were not proportional to the surface coverage due to influences of the guest molecules on the structure, orientation or polariza-

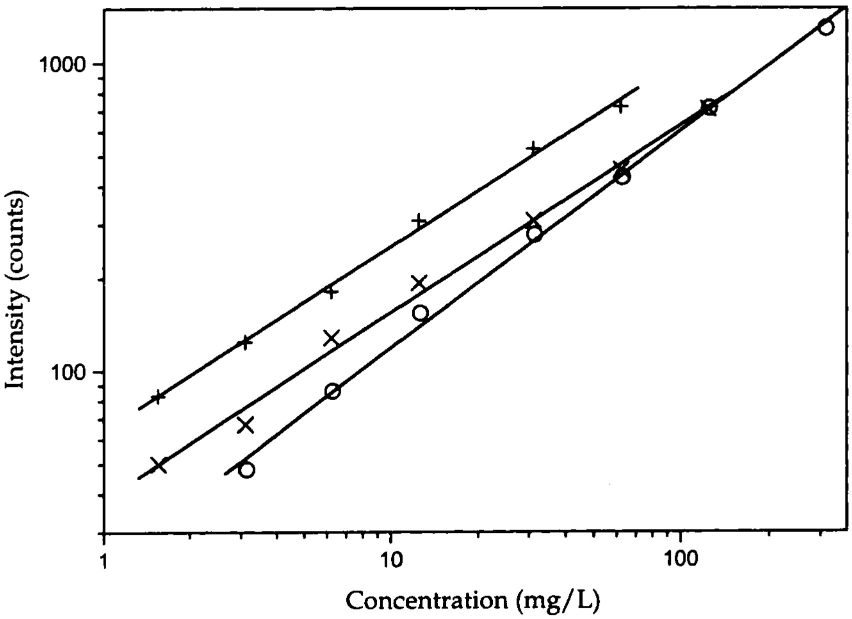

FIGURE 4 SERS band heights as a function of concentration: benzene at 992 cm^{-1}(o), toluene at 1002 cm^{-1}(x). and ethylbenzene at 1003 cm^{-1}(+). All measurements were related to the height of the BCAT band at 1037 cm^{-1}. Band heights of toluene and ethylbenzene were determined using difference spectra with substrates under nitrogen because of an overlap of the analyte bands with a weak band of BCAT

bility of the BCAT host molecules, the bands of which were used as internal standard.

Selectivity

The signal intensities obtained of the different compounds can be used to estimate the selectivity of adsorption. The intensities of the considered SERS bands of *m*- and *o*-xylene as well as of toluene are approximately one and a half that of ethylbenzene and benzene and nearly twice that of *p*-xylene at comparable gas concentrations. Raman measurements of the pure liquid aromatic compounds showed that the scattering cross section of the benzene band is about three to four times larger than that of the bands of the other substances. Neglecting orientational effects and changes of the cross sections due to adsorption, the ratios of surface coverages at similar gas concentrations can be roughly estimated. The coverage with benzene was clearly lower than that with all other substances: the relative coverages in relation to benzene were 5.5 for m-xylene, 3.8 for o-xylene

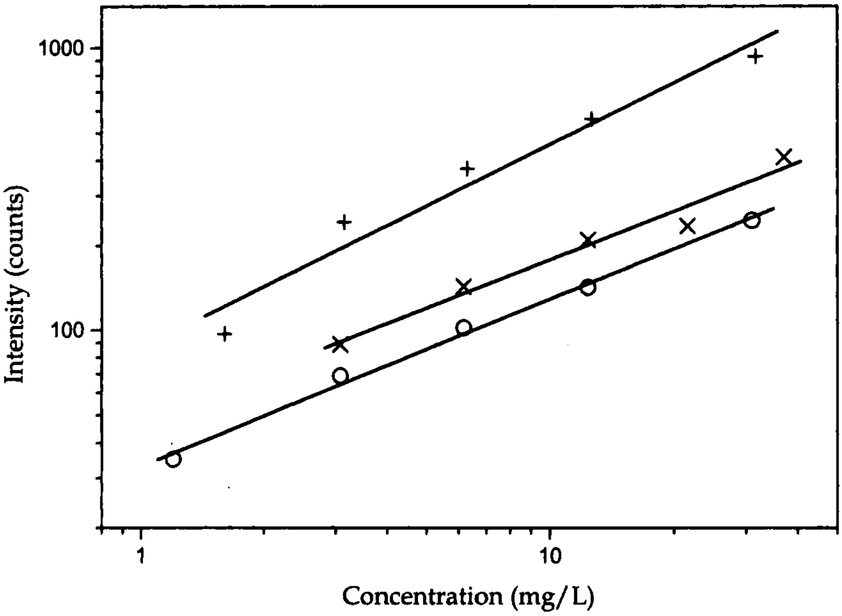

FIGURE 5 SERS band heights as a function of concentration of the isomers of xylene at 734 cm^{-1} (o-xylene, +), 725 cm^{-1} (m-xylene, o), and 825 cm^{-1} (p-xylene, ×). All measurements were related to the height of the BCAT band at 1037 cm^{-1}

and toluene, 3.3 for ethylbenzene and 2.8 for p-xylene. Despite all uncertainties of this estimate, it is evident that the BCAT coated substrates adsorb preferably derivatives with alkyl groups, and that the adsorption also depends on the sterical arrangement of the substituents.

A similar order of selectivity was already observed for the adsorption of benzene and its chloro derivatives from aqueous solutions[5]: an increasing number of substituents led to lower limits of detection. It could not be decided by the experiments in aqueous medium, whether this lowering of limits of detection was due to a preferred interaction of BCAT with the chloro compounds or simply due to an inverse relationship between adsorption and solubility. The present investigations on adsorption from the gas phase, however, demonstrate that there really exists a substituent-dependent interaction with immobilised BCAT at least for alkyl derivatives.

Signal development with time and reversibility of adsorption

Figure 6 shows that the full height of benzene and toluene bands is reached within one to two minutes after application of the analytes. The band heights decrease within the same period after switching to pure nitrogen. The same temporal behaviour was observed for the adsorption of the other four analytes.

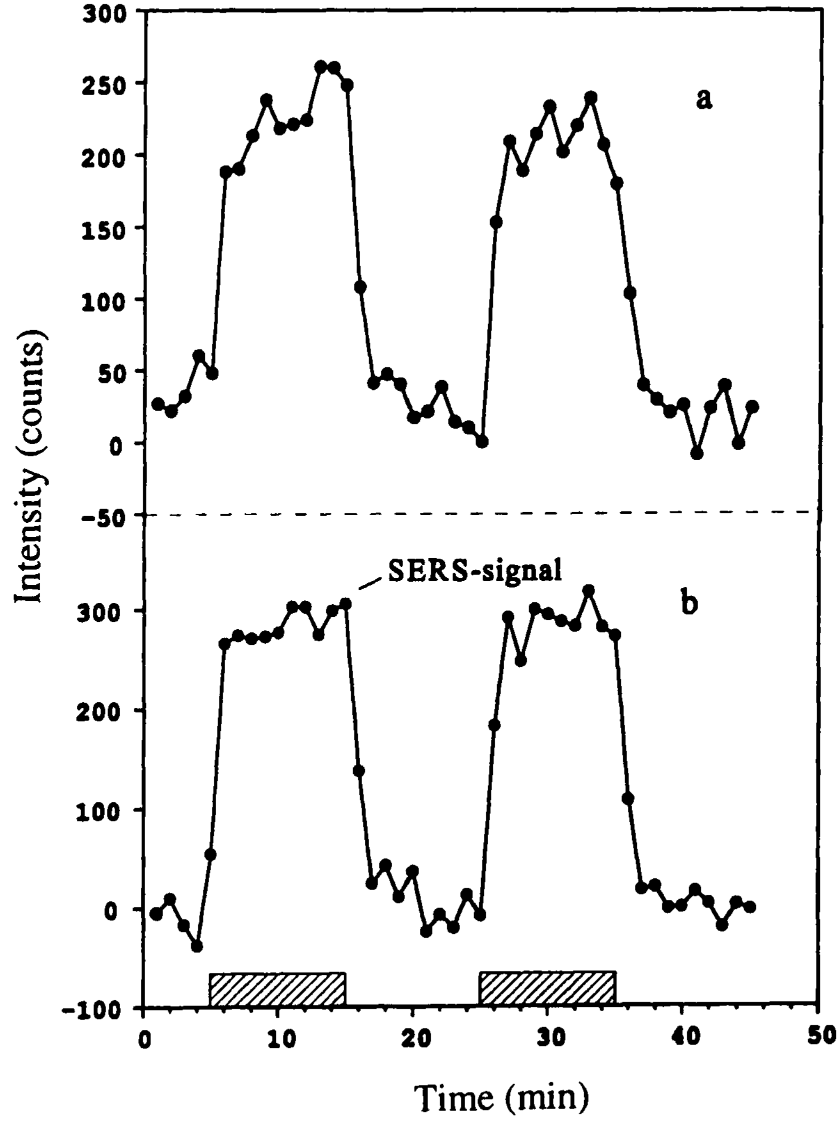

FIGURE 6 Time dependence of the SERS-signals of adsorbed benzene and toluene. Curve a gives the height of the benzene band at 992 cm^{-1}, whereas curve b represents the 1002 cm^{-1} band of toluene. Substrates were exposed to gas concentrations of 31.4 mg/L benzene and 62.2 mg/L of toluene, respectively, during the periods indicated by the hatched areas

An integration time of one minute was necessary to achieve reasonable signal to noise ratios with the spectrometer, which was not optimised for fast measurements. Presently, this integration period limits the time resolution of the measurements. Changes in surface concentrations may proceed even faster than represented by the curves.

Nevertheless, the results demonstrate that SERS at BCAT coated substrates can be useful for highly selective on-line detection of aromatics in the gas phase. The response behaviour of substrates coated with the ultrathin BCAT layers is determined by the adsorption step itself, which obviously proceeds rather fast. Therefore, such layers may be superior to thicker polymeric coatings used in several chemical sensors where diffusion limits the response.

The bands of all analytes disappear completely after switching to pure nitrogen. This complete reversibility is required in sensor applications in order to obtain a definite relationship between the signals measured and the present analyte concentrations.

Adsorption from mixtures

In principle, SERS of aromatic analytes adsorbed at BCAT coated substrates may be used for the detection of components in gas mixtures, since the locations of the bands clearly depend on the number, position and nature of the substituents. All the investigated aromatics, however, are adsorbed by the same host molecules. Therefore, occupation of adsorption places by one species can influence the adsorption of others. Detailed knowledge on the calibration curves for mixtures would be required for quantification of their components.

Co-adsorption of benzene and toluene as a function of the toluene concentration was investigated as an example of adsorption from mixtures (Figure 7). Toluene signals increased nearly linearly with the gas concentration as was observed without benzene being present. Only the last point was somewhat lower than expected, which might indicate beginning saturation. The benzene signals were clearly lowered already by small toluene concentrations. Nearly half of the benzene signal intensity, however, remains when applying the highest toluene concentrations. Apparently, low concentrations of the preferentially adsorbed toluene affect the adsorption of benzene strongly, whereas benzene has little influence on the toluene adsorption..

CONCLUSIONS

BCAT coated SERS substrates adsorb BTXE aromatics from the gas phase fast and fully reversible. Therefore, these substrates can serve for a continuous

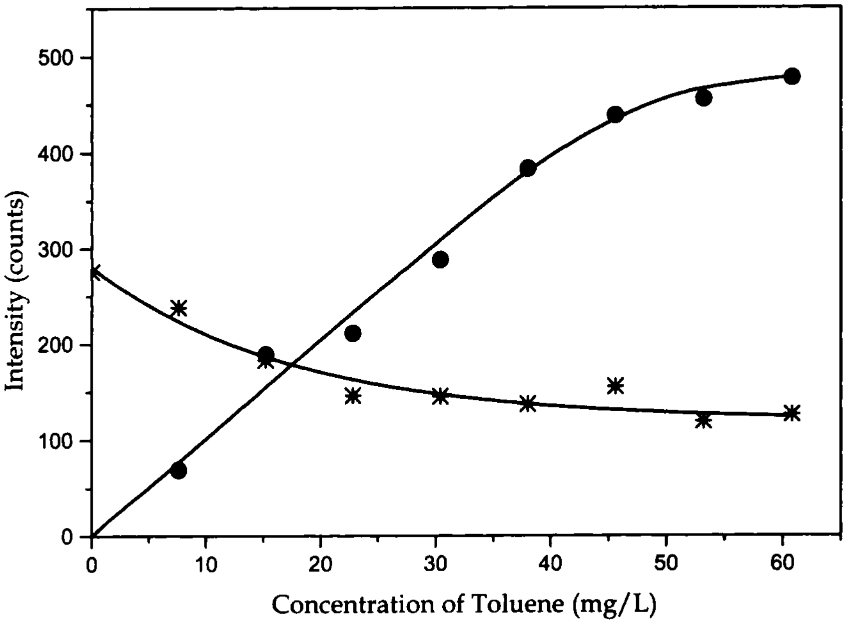

FIGURE 7 Band heights of benzene at 992 cm^{-1} (*) and of toluene at 1002 cm^{-1} (●) for a fixed benzene concentration of 31.4 mg/L and varying toluene concentrations

on-line detection and determination of the investigated aromatic compounds in gaseous media with limits of detection around 2 mg/L. Band heights at the same gas concentration are quite similar for all BTXE aromatics, which is apparently due to a preferred adsorption of alkyl aromatics and the large scattering cross section of benzene.

Acknowledgements

The authors thank C. G. Gibbs and C. D. Gutsche, Texas Christian University, Fort Worth, for the synthesis of BCAT. This work was financially supported by the Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen, the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie, and the network "ENVIROTRACE" within the program "Human Capital and Mobility" of the European Community.

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