(1) Monitoring of polycyclic aromatic hydrocarbons in water using headspace solid-phase microextraction and capillary gas chromatography, Djozan_D, Assadi_Y, UNIV TABRIZ, FAC CHEM, DEPT ANALYT CHEM, TABRIZ, IRAN, MICROCHEMICAL JOURNAL, 1999, Vol.63, No.2, pp.276-284. A laboratory-made fused silica fiber coated with a porous layer of activated charcoal (PLAC) was used as a new microsolid, phase in solid-phase microextraction (SPME) mode for sampling of polycyclic aromatic hydrocarbons (PAHs) from the headspace of water samples. Effects of temperature, salt addition, stirring speed, and exposure time on extraction efficiency were investigated. Extraction at 80 degrees C for 30 min in the presence of 12 g NaCl at constant stirring speed yields maximum efficiency. Using the proposed microsolid phase as an efficient sampling device and capillary gas chromatography with flame ionization detection, reliable determination of these compounds at sub-parts-per-billion concentrations was achieved. The calibration graphs were linear in the range 0.1-50 ng/ml and the detection limits were 0.03-0.3 ng/ml. The proposed method was successfully applied to the determination of PAHs in environmental samples such as local municipal water.

(2) Electrospray mass spectrometry of trimethyllead and triethyllead with in-tube solid phase microextraction sample introduction, Mester_Z, Pawliszyn_J, UNIV WATERLOO, DEPT CHEM, WATERLOO, ON, N2L 3G1, CANADA, RAPID COMMUNICATIONS IN MASS SPECTROMETRY, 1999, Vol.13, No.20, pp.1999-2003. IS: 0951-4198 DT: Article AB: A study of positive ionization electrospray mass spectrometry (ES-MS) was performed on trimethyllead (TML) and triethyllead (TEL). The system consisted of in-tube solid phase microextraction (SPME) coupled directly to an electrospray mass spectrometer. Fragmentation patterns of compounds were observed by applying different fragmentation voltages. High voltages produced sufficient fragmentation to elucidate the dissociation of the trialkyllead compounds. Electrospray mass spectrometry has been shown to be a suitable detection system for organolead speciation. Applying fragmentation energy programming, it might be possible to obtain in parallel the molecular and atomic signals of lead compounds.

(3) Extraction and analysis of polycyclic aromatic hydrocarbons (PAHs) by solid phase micro-extraction/supercritical fluid chromatography (SPME/SFC), Lesellier_E, IUT ORSAY, LETIAM, PLATEAU MOULON, F-91400 ORSAY, FRANCE, ANALUSIS, 1999, Vol.27, No.4, pp.363-368. Solid phase micro-extraction (SPME) is a clean and simple pre-concentration method. Previously used for trace analysis of volatil compounds, the use of SPME was extended to non volatil molecules with the development of an SPME / HPLC interface. This new interface allows the extraction and the analyses of high molecular weight compounds found in aqueous samples. Since supercritical fluid chromatography is particularly well suited for analysis of complex mixtures containing non volatil compounds, the feasibility of coupling SPME and SFC has been investigated and applied to PAHs. Several points have been studied:
i/ behavior of interface and of fiber to supercritical fluid and high pressure required by the analytical method; ii/ kind of the compounds transfer from the fiber to the analytical column; iii/ relation between the nature of the fibers and the quantity of extracted compounds; iii/ effect of salt addition. The results show that the SPME / SFC technic may be used for extraction and analysis of PAHs, since the quantity of extracted compounds reaches 30%.

(4) Biomarkers of dose and susceptibility in cyclists exposed to monoaromatic hydrocarbons, Bergamaschi_E, Brustolin_A, DePalma_G, Manini_P, Mozzoni_P, Andreoli_R, Cavazzini_S, Mutti_A, UNIV PARMA, SCH MED, LAB IND TOXICOLO, VIA A GRAMSCI 14, I-43100 PARMA, ITALY JN: TOXICOLOGY LETTERS, 1999, Vol.108, No.2-3, pp.241-247. Article AB: A quasi-experimental held study was carried out in 24 volunteers with the aim of: (i) assessing personal exposure to aromatic hydrocarbons polluting urban areas; and (ii) exploring the role of polymorphic enzymes relevant to the biotransformation of benzene in the inter-individual variability of biomarkers. Each subject covered by bicycle: (i) inner city routes with often jammed traffic; and (ii) open rural routes. Time-weighted average airborne concentrations of benzene, toluene, ethylbenzene and xylenes (BTEX) were determined during 2-h runs. BTEX were determined by solid-phase microextraction (SPME) followed by gas chromatography coupled with mass spectrometry (GC-MS) in blood and spot urine samples collected just before and immediately after the runs. Urinary t,t-muconic acid was measured by high performance liquid chromatography (HPLC)-UV. Genotypes of epoxide hydrolase (EH) and glutathione-S-transferase class mu-1 (GSTM1) were also characterised. As compared to pre-run values, benzene and toluene in blood, and toluene and xylenes in urine significantly increased after urban runs. Urinary t,t-muconic acid was significantly higher in post-run samples after both urban (P < 0.001) and rural runs (P < 0.05). Despite a narrow range of exposure levels, a significant relationship was observed between airborne benzene and post-run t,t-muconic acid (r(2) = 0.349, P < 0.001). When subgroups were distinguished according to EH and GSTM1, subjects bearing both the EH wild type and GSTM 'null' genotype showed significant exposure-related changes in t,t-muconic acid excretion. Even at very low exposure levels, a 2-h bike run in a polluted urban environment may give rise to measurable changes in biomarkers of internal dose of selected aromatic hydrocarbons. Genetically-based metabolic differences may account for part of the inter-individual variability of biomarkers of exposure.

(5) Simple analysis of arylamide herbicides in serum using headspace-solid phase microextraction and GC/MS, Namera_A, Watanabe_T, Yashiki_M, Iwasaki_Y, Kojima_T, HIROSHIMA UNIV, SCH MED, DEPT LEGAL MED, MINAMI KU, 1-2-3 KASUMI, HIROSHIMA 7348551, JAPAN, FORENSIC SCIENCE INTERNATIONAL, 1999, Vol.103, No.3, pp.217-226. A simple and sensitive method for analysis of four arylamide herbicides (butachlor, propanil, diphenamide and propyzamide) in serum was developed using a headspace-solid phase microextraction (SPME) and a gas chromatograph-mass spectrometer (GC-MS). A vial containing a serum sample and sodium chloride was heated at 90 degrees C. The extraction fiber of the SPME was exposed for 45 min in the headspace of the vial. The compounds adsorbed on the fiber were desorbed by exposing the fiber in the injection port of the GC-MS. The calibration curves, using an internal standard method, demonstrated good Linearity throughout the concentration range from 0.25 to 10.0 μg/ml. Propyzamide was used for an internal standard. The limit of detection was 0.10, 0.05, and 0.25 μg/ml for butachlor,
diphenamide, and propanil, respectively. No interferences were found, and the time for analysis was 60 min for one sample. In addition, this proposed method was applied to a suicide case in which the patient ingested Kusanon A(R), a herbicide. Propanil, which was the main ingredient in the herbicide, was detected in the eight serum samples collected from the patient during the hospitalization at the concentration range from 26.7 to 1.1 μg/ml.

(6) A simple method for the extraction of volatile organic compounds contained in air samples from adsorbent materials by solid phase microextraction and their analysis by gas chromatography / mass spectrometry, Saba_A, Raffaelli_A, Pucci_S, Salvadori_P, UNIV PISA, DIPARTIMENTO CHIM & CHIM IND, CTR STUDIO MACROMOL STEREORDINATE & OTTICAMENTE A, CNR, I-56126 PISA, ITALY, RAPID COMMUNICATIONS IN MASS SPECTROMETRY, 1999, Vol.13, No.19, pp.1899-1902. The monitoring of air pollution requires simple, rapid and sensitive sampling and analytical techniques that are usable for routine analyses. In our laboratories we have developed a method for the analysis of air samples collected by adsorbent cartridges based on solid phase microextraction (SPME) coupled to gas chromatography/mass spectrometry. We investigated the influence of some variables (time and temperature) using toluene as analyte (one of the most common air pollutants) and toluene-d(8) on the SPME extraction, and the sensitivity (LOQ) of the method. We then tested the method on an air sample collected in an industrial area and carried out characterisation of the volatile organic compounds present.

(7) Automated in tube solid-phase microextraction coupled with liquid chromatography/electrospray ionization mass spectrometry for the determination of beta-blockers and metabolites in urine and serum samples, Kataoka_H, Narimatsu_S, Lord_HL, Pawliszyn_J, UNIV WATERLOO, DEPT CHEM, WATERLOO, ON N2L 3G1, CANADA OKAYAMA UNIV, FAC PHARMACEUT SCI, OKAYAMA 7008530, JAPAN, ANALYTICAL CHEMISTRY, 1999, Vol.71, No.19, pp.4237-4244. The technique of automated in-tube solid-phase microextraction (SPME) coupled with liquid chromatography/electrospray ionization mass spectrometry (LC/ESI-MS) was evaluated for the determination of beta-blockers in urine and serum samples. In-tube SPME is an extraction technique for organic compounds in aqueous samples, in which analytes are extracted from the sample directly into an open tubular capillary by repeated draw/eject cycles of sample solution. LC/MS analyses of beta-blockers were initially performed by liquid injection onto a LC column. Nine beta-blockers tested in this study gave very simple ESI mass spectra, and strong signals corresponding to [M + H](+) were observed for all beta-blockers. The beta-blockers were separated with a Hypersil BDS C-18 column using acetonitrile/methanol/water/acetic acid (15:15:70:1) as a mobile phase. To optimize the extraction of beta-blockers, several in-tube SPME parameters were examined. The optimum extraction conditions were 15 draw/eject cycles of 30 μL of sample in 100 mM Tris-HCl (pH 8.5) at a flow rate of 100 μL/min using an Omegawax 250 capillary (Supelco, Bellefonte, PA). The beta-blockers extracted by the capillary were easily desorbed by mobile-phase flow, and carryover of beta-blockers was not observed. Using in-tube SPME/LC/ESI-MS with selected ion monitoring, the calibration curves of beta-blockers were linear in the range from 2 to 100 ng/mL with correlation coefficients above 0.9982 (n = 18) and detection limits (S/N = 3) of 0.1-1.2 ng/mL. This method was successfully applied to the analysis of biological samples without interference peaks. The recoveries of beta-blockers spiked
into human urine and serum samples were above 84 and 71%, respectively. A serum sample from a patient administrated propranolol was analyzed using this method and both propranolol and its metabolites were detected.

(8) Application of headspace solid-phase microextraction to volatile flavour profile development during storage and ripening of kiwifruit, Wan_XM, Stevenson_RJ, Chen_XD, Melton_LD, UNIV AUCKLAND, DEPT CHEM, AUCKLAND 1, NEW ZEALAND UNIV AUCKLAND, DEPT CHEM & MAT ENGN, FOOD SCI & PROC ENGN GRP, AUCKLAND, NEW ZEALAND, FOOD RESEARCH INTERNATIONAL, 1999, Vol.32, No.3, pp.175-183 IS: 0963-9969. Kiwifruit volatile flavour compounds were evaluated with headspace solid-phase microextraction (SPME) as a sample concentration technique. Gas chromatography-mass spectrometry (GC-MS) was used for qualitative and semi-quantitative analysis after SPME. Components such as heptanal, ethyl hex-3-enoate, 6- methylhept-5-en-2-one, acetic acid, c/t-2-nonenal (mixture) and c t-2-decenal (mixture), which were previously found only in kiwifruit juice, were detected by headspace SPME-GC-MS. Other compounds (pent-4-enal, t,t-nona-2,4-dienal, 2-nonanone, ethyl octanoate, butyrolactone and 2-propenyl butanoate), which had not been found previously, were identified. Flavour volatiles of kiwifruit were very sensitive to storage time and state of ripeness.

(9) Monoterpene composition of essential oil from peppermint (Mentha x piperita L.) with regard to leaf position using solid-phase microextraction and gas chromatography/mass spectrometry analysis, Rohloff_J, NORWEGIAN UNIV SCI & TECHNOL, DEPT BOT, PLANT BIOCTR, N-7491 TRONDHEIM, NORWAY, JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY, 1999, Vol.47, No.9, pp.3782-3786. Monoterpene compounds of leaf pairs and flowers of Mentha x piperita have been studied by direct headspace sampling using solid-phase microextraction coupled with gas chromatography / mass spectrometry (SPME-GC/MS). The content of peppermint-characteristic compounds such as menthol, menthyl acetate, and neomenthol increased in a basipetal direction (older plant parts), whereas menthone and isomenthone showed higher levels in the acropetal direction (younger plant parts). Higher levels of menthofuran were found in peppermint flowers in contrast to the leaves. SPME sampling resulted in relatively higher amounts of high-volatile monoterpenes and lower detection of less volatile compounds such as menthol and menthone, compared to solvent-based samples from essential oil distillation.

(10) Molecular and isotopic analysis of oils by solid phase microextraction of gasoline range hydrocarbons, Harris_SA, Whiticar_MJ, Eek_MK, UNIV VICTORIA, SCH EARTH & OCEAN SCI, VICTORIA, BC V8W 2Y2, CANADA, ORGANIC GEOCHEMISTRY, 1999, Vol.30, No.8A, pp.721-737. An improved method for molecular and stable isotope analysis of gasoline range hydrocarbons (C-5-C-10) in oils uses Solid Phase Microextraction. Analytes are sampled from the headspace above oil droplets and analyzed by gas chromatography and continuous- flow isotope-ratio mass spectrometry. Analytical considerations with this sampling technique include equilibration times, vapor pressure/temperature effects, and the presence of a complex matrix. Instrumentation factors such as column/split flows are also considered. The results are compared with an alternative purge and trap method. Molecular analyses prove reproducible between the two methods, however, stable carbon isotope ratios exhibit a non-systematic depletion and enrichment of 0.2-2.0 parts per thousand for 16 pre-selected compounds.
(11) SPME-HPLC analysis of Allium lacrymatory factor and thiosulfinates, Jaillais_B, Cadoux_F, Auger_J, UNIV TOURS, FAC SCI & TECH,IRBL,PARC DE GRANDMONT, F-37200 TOURS, FRANCE UNIV TOURS, FAC SCI & TECH,IRBLF-37200 TOURS,FRANCE RP TEXEL,F-86220 DANGE ST ROMAIN, FRANCE, TALANTA, 1999, Vol.50, No.2, pp.423-431 .The commercial SPME-HPLC interface is investigated to improve the analysis of Allium volatiles. Volatiles trapped by liquid nitrogen were previously transferred to RP-HPLC by a classical injection. In this work we compare the results obtained with classical injection and SPME used in headspace mode. This SPME- HPLC interface can be used when it is important to spare the sample, but thiosulfinates are partially degraded.

(12) Determination of polynuclear aromatic hydrocarbons in human blood serum by proteolytic digestion - direct immersion SPME, Poon_KF, Lam_PK, Lam_MHW, CITY UNIV HONG KONG,DEPT BIOL & CHEM,CTR COASTAL POLLUT & CONSERVAT,TAT CHEE AVE,KOWLOON,HONG KONG CITY UNIV HONG KONG,DEPT BIOL & CHEM,CTR COASTAL POLLUT & CONSERVAT,KOWLOON,HONG KONG, ANALYTICA CHIMICA ACTA, 1999, Vol.396, No.2-3, pp.303-308 . A proteolytic digestion - direct immersion solid phase microextraction (SPME) method has been developed for the determination of polynuclear aromatic hydrocarbons in human blood serum. Non-specific serine protease, Proteinase K, was employed to remove the fouling of the SPME stationary phase:by the lipoprotein in blood serum during extraction. Optimization of protease concentration and duration of the proteolytic digestion as well as SPME sampling have been performed. Proteinase K concentration of 190 μg protease/ml of serum and digestion time of 60 min at 25 degrees C were found to be the optimum conditions for the determination. PAH recoveries of the direct immersion SPME method ranged from 81.1 to 98.5%. The relative repeatability of the method was found to be 5.6% (n = 10). Detection limits for the 16 prioritized PAHs ranged from 2.7 to 30.4 ppb.

(13) Solid-phase microextraction gas chromatographic-mass spectrometric method for the determination of inhalation anesthetics in urine, Poli_D, Bergamaschi_E, Manini_P,Andreoli_R, Mutti_A, UNIV PARMA,DIPARTIMENTO CLIN MED NEFROL & SCI PREVENZ,LAB TOSSICOL IND,VIA GRAMSCI 14,1-43100 PARMA, ITALY UNIV PARMA, DIPARTIMENTO CLIN MED NEFROL & SCI PREVENZ,LAB TOSSICOL IND,1-43100 PARMA,ITALY, JOURNAL OF CHROMATOGRAPHY B, 1999, Vol.732, No.1, pp.115-125 .Solid-phase microextraction (SPME) has been applied to the headspace sampling of inhalation anesthetics (i.e. nitrous oxide, isoflurane and halothane) in human urine. Analysis was carried out by gas chromatography-mass spectrometry using a capillary column with a divinylbenzene porous polymeric stationary phase, A SPME divinylbenzene-Carboxen-polydimethylsiloxane coated fiber, 2 cm long, was used, and its performances were compared with those of a Carboxen-PDMS in terms of sensitivity, extraction efficiency, extraction time, fiber coating-urine distribution coefficient. For both fibers, linearity was established over four orders of magnitude, limits of detection were below 100 ng/l for nitrous oxide and below 30 ng/l for halogenated. Precision calculated as %RSD was within 3-13% for all intra- and inter-day determinations. The method was applied to the quantitative analysis of anesthetics in the urine of occupationally exposed people (operating room personnel).
Factors influencing leucine catabolism by a strain of Staphylococcus carnosus, Masson_F, Hinrichsen_L, Talon_R, Montel_MC, INRA, STN RECH VIANDE, MICROBIO LAB, F-63122 ST GENES CHAMPANE, FRANCE DANISH MEAT RES INST, DK-4000 ROSKILDE, DENMARK, INTERNATIONAL JOURNAL OF FOOD MICROBIOLOGY, 1999, Vol.49, No.3, pp.173-178. The metabolism of leucine by resting cells of Staphylococcus carnosus 833 was studied according to three physicochemical factors: culture condition (defined medium: complex medium), nitrate concentration (0% and 0.03%) and stirring condition (static or shaking). A factorial design as set up to test the effects of these factors, each at two levels. The results showed that resting cells of S. carnosus 833 produced 3-methyl butanal, 3-methyl butanol and 3-methyl butanoic acid from leucine. Whatever the incubation conditions, there was greater quantity of 3-methyl butanoic acid than 3-methyl butanal and 3-methyl butanol. The preculture and incubation conditions influenced the level of production of the 3 metabolites. The highest overall production of the 3 metabolites was observed when cells were incubated without nitrate in the reaction mixture. 3-methylbutanoic acid production was enhanced when S. carnosus 833 was precultivated in complex medium. 3-methylbutanal was only detected when cells were precultivated in defined medium. Stirring condition had no effect on leucine catabolism of S. carnosus 833.

Rapid analysis of tetracycline antibiotics by combined solid phase microextraction/high performance liquid chromatography / mass spectrometry, Lock_CM, Chen_L, Volmer_DA NA: NATL RES COUNCIL, INST MARINE BIOSCI, 1411 OXFORD ST, HALIFAX, NS B3H 3Z1, CANADA MERCK KGAA, ANALYT RES ZF A ZFA, D-64271 DARMSTADT, GERMANY, RAPID COMMUNICATIONS IN MASS SPECTROMETRY, 1999, Vol.13, No.17, pp.1744-1754. The technique of solid phase microextraction (SPME) combined on-line with high performance liquid chromatography/mass spectrometry (HPLC/MS) has been applied to the analysis of seven tetracycline analogues. Rapid baseline separation was achieved in under 5 min using a short 3 mm RP-18e cartridge column. Optimisation of the SPME procedure is described including choice of extracting fibre and modification of the sample by heating or salting out of the analytes. Detection limits of 4-40 ng/mL were obtained for the various analogues from extracted aqueous samples and absolute amounts of analyte extracted by the method determined using external calibration. To demonstrate the applicability of the technique for real samples the extraction of tetracycline from milk is described.

Gas chromatographic-mass spectrometric analysis of dichlorobenzene isomers in human blood with headspace solid-phase microextraction Liu_JT, Hara_K, Kashimura_S, Hamanaka_T, Tomojiiri_S, Tanaka_K, FUKUOKA UNIV, SCH MED, DEPT FORENS MED, JONAN KU, 7-45-1 NANAKUMA, FUKUOKA 8140180, JAPAN FUKUOKA UNIV, SCH MED, DEPT FORENS MED, JONAN KU, FUKUOKA 8140180, JAPAN FUKUOKA UNIV, SCH MED, DEPT EMERGENCY & CRIT CARE MED, JONAN KU, FUKUOKA 8140180, JAPAN CHINA MED UNIV, DEPT FORENS CHEM, SHENYANG 110001, PEOPLES R CHINA, JOURNAL OF CHROMATOGRAPHY B, 1999, Vol.731, No.2, pp.217-221. Headspace solid-phase microextraction (HS-SPME) was utilized for the determination of three dichlorobenzene isomers (DCBs) in human blood. In the headspace at 30 degrees C, DCBs were absorbed for 15 min by a 100-mm polydimethylsiloxane (PDMS) fiber. They were then analyzed by capillary column gas chromatography-mass
spectrometry (GC-MS). By the initial column oven temperature at 20 degrees C, the three isomers were resolved at the baseline level, p-Xylene-d(10) was used as the internal standard (L.S.). For quantitation, the molecular ion at m/z 146 for each isomer and the molecular ion at m/z for I.S. were selected. For day-to-day precision, relative standard deviations in the range 3.2-10.7% were found at concentrations of 1.0 and 10 μg/ml. Each compound was detectable at a level of at least 0.02 μg per 1g of whole blood full mass scanning. HS-SPME-GC-MS, when performed at relatively low temperatures, was found to be feasible toxicological laboratories. Using this method, the plasma levels of one patient who had drunk a pesticide-like material measured.

(17) Fishing for a drug: solid-phase microextraction for the assay of clozapine in human plasma, Ulrich_S, Kruggel_S, Weigmann_H, Hiemke_C, OTTO VON GUERICKE UNIV,UNIV HOSP,INST CLIN PHARMACOL, LEIPZIGER STR 44,D-39120 MAGDEBURG,GERMANY UNIV MAINZ, UNIV HOSP, PSYCHIAT CLIN,D-55101 MAINZ,GERMANY, JOURNAL OF CHROMATOGRAPHY B, 1999, Vol.731, No.2, pp.231-240 IS: 0378-4347. Solid-phase microextraction (SPME) was investigated as a sample preparation method for assaying the neuroleptic drug clozapine in human plasma. A mixture of human plasma, water; loxapine (as internal standard) and aqueous NaOH was extracted with a 100-μm polydimethylsiloxane (PDMS) fiber (Supelco). Desorption of the fiber was performed in the injection port of a gas chromatograph at 260 degrees C (HP 5890; 30 mx0.53 mm I.D., 1 μm film capillary; nitrogen-phosphorous selective detection). Fibers were used repeatedly in up to about 75 analyses. The recovery was found to be 3% for clozapine from plasma after 30 min of extraction. However, in spite of the low recovery, the analyte was well separated and the calibration was linear between 100 and 1000 ng/ml. The within-day and between-day precision was consistently about 8 to 15% at concentrations of 200 ng/ml to 1000 ng/ml. No interfering drug was found. The limit of detection was 30 ng/ml. The sample volume was 250 μl. The influence of the concentration of proteins, triglycerides and salt, i.e., changes in the matrix on the peak areas and peak-area ratios was studied. The method is not impaired by physiological changes in the composition of the matrix. Good agreement was found with a liquid-liquid extraction-gas-liquid chromatography (LLE-GLC) standard method and an on-line column-switching high-performance liquid chromatography (HPLC) method for patients’ samples and spiked samples, respectively. It is concluded that the method can be used in the therapeutic drug monitoring of clozapine because the therapeutic window of clozapine is from 350 to 600 ng/ml.

(18) Automated in-tube solid-phase microextraction-liquid chromatography-electrospray ionization mass spectrometry for the determination of ranitidine, Kataoka_H, Lord_HL, Pawliszyn_J. UNIV WATERLOO,DEPT CHEM,WATERLOO,ON N2L 3G1,CANADA, JOURNAL OF CHROMATOGRAPHY B, 1999, Vol.731, No.2, pp.353-359. The technique of automated in-tube solid-phase microextraction (SPME) coupled with liquid chromatography-electrospray ionization mass spectrometry (LC-ESI-MS) was evaluated for the determination of ranitidine. In-tube SPME is an extraction technique for organic compounds in aqueous samples, in which analytes are extracted from the sample directly into an open tubular capillary column by repeated aspirate/dispense steps. In order to optimize the extraction of ranitidine, several in-tube SPME parameters such as capillary column stationary phase, extraction pH and number and volume of aspirate/dispense steps were investigated. The optimum extraction conditions for ranitidine from aqueous samples were 10 aspirate/dispense steps of 30 μl of sample in
25 mM Tris-HCl (pH 8.5) with an Omegawax 250 capillary column (60 cm x 0.25 mm LD., 0.25 μm film thickness). The ranitidine extracted on the capillary column was easily desorbed with methanol, and then transported to the Supelcosil LC-CN column with the mobile phase methanol-2-propanol-5 M ammonium acetate (50:50:1). The ranitidine eluted from the column was determined by ESI-MS in selected ion monitoring mode. In-tube SPME followed by LC-ESI-MS was performed automatically using the HP 1100 autosampler. Each analysis required 16 min, and carryover of ranitidine in this system was below 1%. The calibration curve of ranitidine in the range of 5-1000 ng/ml was linear with a correlation coefficient of 0.9997 (n=24), and a detection limit at a signal-to-noise ratio of three was ca. 1.4 ng/ml. The within-day and between-day variations in ranitidine analysis were 2.5 and 6.2% (n=5), respectively. This method was also applied for the analyses of tablet and urine samples.

(19) Development of a solid phase microextraction method for detection of the use of banned azo dyes in coloured textiles and leather, Cioni_F, Bartolucci_G, Pieraccini_G, Meloni_S, Moneti_G, UNIV FLORENCE, CISM, VIALE G PIERACCINI 6, I-50134 FLORENCE, ITALY UNIV FLORENCE, CISM, I-50134 FLORENCE, ITALY ARPAT, DIPARTIMENTO PROV FIRENZE, I-50144 FLORENCE, ITALY IST TECN IND Q SELLA, LAB ANAL & CONTROLLO QUAL, I-13900 BIELLA, ITALY, RAPID COMMUNICATIONS IN MASS SPECTROMETRY, 1999, Vol.13, No.18, pp.1833-1837. A new method to detect the use of banned azo dyes in the manufacture and treatment of coloured textiles and leather is described. The determination of the azo dyes was made by quantification of aromatic amines generated by reductive cleavage in a citrate buffer medium. The aromatic amines were then extracted from 1 ml of the reaction solution by means of solid phase microextraction (SPME) and determined by gas chromatography/mass spectrometry (GC/MS). We also evaluate accuracy, precision, range of linearity and limit of detection for the eighteen aromatic amines investigated, and show that the method is comparable with current established methods.

(20) Rapid analysis of parathion in biological samples using headspace solid-phase micro-extraction (HS-SPME) and gas chromatography/mass spectrometry (GC/MS), Musshoff_F, Junker_H, Madea_B, UNIV BONN, INST LEGAL MED, STIFTSPL 12, D-53111 BONN, GERMANY, CLINICAL CHEMISTRY AND LABORATORY MEDICINE, 1999, Vol.37, No.6, pp.639-642. A simple and rapid method for the analysis of parathion in biological samples is presented. The method consists of the extraction of parathion from blood samples by headspace solid-phase micro-extraction (SPME), followed by capillary gas chromatography and mass spectrometry detection. The recoveries in the blood samples after addition of ammonium sulphate and sulphuric acid were between 85% and 89% compared to samples prepared in water. Linearity was established over a concentration range of 0.1-5 μg/g blood with acceptable coefficients of correlation and limits of detection reached 0.02-0.05 μg/g. The time for an analysis is 57 minutes for one sample, including the extraction step. In conclusion, HS-SPME in combination with GC/MS is an effective method for the determination and quantification of parathion-ethyl and parathion-methyl in biological material.

Act bans the use of methyl bromide after 2005. Consequently, the development of alternative methods for control of soilborne pathogens is imperative. One alternative is to exploit the pesticidal properties of Brassica L. species. Macerated leaves (10 g) from 'Premium Crop' broccoli [B. oleracea L. (Botrytis Group)], 'Charmant' cabbage [B. oleracea L. (Capitata Group)], 'Michihili Jade Pagoda' Chinese cabbage [B. rapa L. (Pekinensis Group)], 'Blue Scotch Curled' kale [B. oleracea L. (Acephala Group)], Indian mustard [B. juncea (L.) Czerniak, unknown cultivar] or 'Florida Broadleaf' mustard [B. juncea (L.) Czerniak] were placed in 500-mL glass jars. Petri dishes with either Pythium ultimum Trow or Rhizoctonia solani Kuhn plugs on potato-dextrose agar were placed over the jar mouths. Radial growth of both fungi was suppressed most by Indian mustard. Volatiles were collected by solid-phase microextraction (SPME) and analyzed by gas chromatography-mass spectrometry. Allyl isothiocyanate (AITC) comprised >90% of the volatiles measured from 'Florida Broadleaf' mustard and Indian mustard whereas (Z)-3-hexenyl acetate was the predominant compound emitted by the other species. Isothiocyanates were not detected by SPME from 'Premium Crop' broccoli and 'Blue Scotch Curled' kale although glucosinolates were found in freeze-dried leaves of all species. When exposed to AITC standard, P. ultimum growth was partially suppressed by 1.1 μmol.L-1 (μmol AITC/headsphere volume) and completely suppressed by 2.2 μmol.L-1. R. solani was partially suppressed by 1.1, 2.2, and 3.3 μmol.L-1 AITC. Use of Brassica species for control of fungal pathogens is promising; the presence of AITC in both lines of B. juncea suppressed P. ultimum and A. solani but some Brassicas were inhibitory even when isothiocyanates were not detected.


(23) Optimization of the SPME device design for field applications AU: Muller_L, Gorecki_T, Pawliszyn_J NA: UNIV WATERLOO,DEPT CHEM,WATERLOO,ON N2L 3G1,CANADA, FRESENIUS JOURNAL OF ANALYTICAL CHEMISTRY, 1999, Vol.364, No.7, pp.610-616, Solid Phase Microextraction (SPME) is a powerful tool for field investigations. With the help of a portable gas chromatograph it can be used for fast analysis directly on-site, or it can be utilized for field sampling and then transported to the laboratory for instrumental analysis. In the latter case, it is important for the reliability of the results that losses of volatiles and contamination of the fiber during storage and transport are minimized. A number of dedicated devices, designed and built for SPME field sampling and storage, have been developed and tested. Sealing capacity of the prototypes was investigated by storing compounds ranging in volatility from methylene chloride to 1,3-dichlorobenzene on selected SPME fibers (100 μm PDMS, 65 μm PDMS/DVB and 75 μm Carboxen/PDMS) at different temperatures. Significant differences were noticed in storage capacity from coating to coating. A comparison between the field samplers optimized in this study and the field sampler commercially available from Supelco revealed advantages and limitations of each of the designs. A gas-tight valve syringe (50 μL SampleLock by Hamilton), modified in order to accommodate the SPME Fiber, had the best storage capacity for very volatile compounds. With this device, over 80% of the initial amount of methylene chloride was retained by the 100 μm PDMS fiber after 24 h of refrigerated storage,
which is a very good result considering that the PDMS coating is characterized by very low storage capacity for volatiles. Field sampling Investigations with the SPME prototypes confirmed the usefulness of these devices for field analysis.

(24) Heterogenic catalytic hydrolysis and analysis of natural pyrethrins in subcritical water coupled with solid phase microextraction (SPME) and GC-MS. Krappe_M, Hawthorne_SB, Wenclawiak_BW, UNIV GESAMTHSCH SIEGEN, ADOLF EICHWEIN STR 2, D-57068 SIEGEN, GERMANY UNIV GESAMTHSCH SIEGEN, D-57068 SIEGEN, GERMANY UNIV N DAKOTA, ENERGY & ENVIRONM RES CTR, GRAND FORKS, ND, 58202, FRESENIUS JOURNAL OF ANALYTICAL CHEMISTRY, 1999, Vol.364, No.7, pp.625-630. The natural pyrethrins, cinerin I, jasmolin I and pyrethrin I, have been hydrolyzed to chrysanthemic acid (CA) in subcritical water in the presence of basic alumina. The hydrolysis and extraction was performed in situ with subcritical water. The conversion to acid is reproducible at 200 degrees C and 30 min with an RSD of 19% (n = 16) at a concentration level of 1.2 x 10(-8) mol/L CA and 12% (n = 12) at concentration level of 1.2 x 10(-7) mol/L CA. An analytical method using Solid Phase Micro Extraction (SPME) combined with GC-FID or -MSD was developed and optimized. For SPME an equilibration time of 20 min at pH of 2 was required. Three fibers, 100 mu m polydimethylsiloxane (PDMS), 85 mu m polyacrylate (PA) and 65 mu m carbowax / divinylbenzene (CW) were evaluated. The Carbowax/divinylbenzene fiber has the highest affinity for CA, but the capacity decreases significantly from experiment to experiment. The most reproducible and most stable one was the PDMS fiber. Two internal standards, octanoic acid and cis-chrysanthemic acid, were used because CA degrades slowly at 200 degrees C in water. This method was applied to analyze some products which contain pyrethrum as an active ingredient, such as insect spray, shampoo against lice, and dried chrysanthemum flowers. The results are comparable to SFC-FID data and correspond to the values given by the manufacturer.

(25) Analysis of volatile varnishes of coated wires by SPME. Hinz_DC, KwartengAcheampong_W, Wenclawiak_BW, UNIV GESAMTHSCH SIEGEN, ADOLF REICHWEIN STR 9, D-57068 SIEGEN, GERMANY UNIV GESAMTHSCH SIEGEN, D-57068 SIEGEN, GERMANY HUK UMWELTLABOR GMBH, D-57482 WENDEN, GERMANY, FRESENIUS JOURNAL OF ANALYTICAL CHEMISTRY, 1999, Vol.364, No.7, pp.641-642. Metal wires coated with varnishes emit organic compounds with increasing of temperature. The use of head-space-GC/MS in the full scan modus is required to identify these compounds. Solid phase microextraction (SPME) allows to analyze the emissions by GC/MS. The response for headspace/SPME-GC/MS is larger than for headspace-GC/FID although the FID, detector is very sensitive.

(28) Determination of VOC contamination in borehole sediments by headspace-SPME-GC analysis. Dermietzel_J, Strenge_G, UFZ CTR ENVIRONM RES LEIPZIG HALLE, DEPT HYDROGEOL, THEODOR LIESER STR 4, D-06120 HALLE, GERMANY, FRESENIUS JOURNAL OF ANALYTICAL CHEMISTRY, 1999, Vol.364, No.7, pp.645-647. VOC contaminants in sediments can be transferred to water by simply shaking water/sediment mixtures until an equilibrium distribution has been reached. The VOC components can then be analysed by solid phase microextraction (SPME) from the headspace of the water phase. Equilibration between equal amounts of sediments and increasing volumes of water allows to use the measured
concentrations in the aqueous phase for the calculation of the concentrations in the sediment, without applying standards.

(27) Solid-phase microextraction for the assay of clozapine in human plasma, Kruggel_S, Ulrich_S, UNIV HOSP, INST CLIN PHARMACOL, LEIPZIGER STR 44, D-39120 MAGDEBURG, GERMANY, FRESENIUS JOURNAL OF ANALYTICAL CHEMISTRY, 1999, Vol. 364, No.7, pp. 654-655. Solid-phase microextraction (SPME) was investigated as sample preparation for the assay of the neuroleptic drug clozapine in human plasma. A mixture of human plasma, water, loxapine as internal standard and aqueous NaOH was extracted with a 100 μm polydimethylsiloxane-(PDMS)-fiber for 30 min. The analyte and internal standard were well separated in the gas chromatogram. The calibration was linear and passed the origin. Accuracy and precision as well as the influence of changes of the matrix were investigated. No interfering drug was found. It is concluded that the method can be used in the therapeutic drug monitoring of clozapine.

(29) Improved extraction of glycol ethers from water by solid-phase micro extraction by carboxen polydimethylsiloxane-coated fiber, Bensoam_J, Cicolella_A, Dujardin_R, INST NATL ENVIRONM IND & RISQUES, BP 2, F-60550 VERNEUIL, FRANCE, CHROMATOGRAPHIA, 1999, Vol. 50, No. 3-4, pp. 155-159. 15 glycol ethers can be extracted from water by solid-phase microextraction with a carboxen-polydimethylsiloxane and separated by GC a Carbowax column. Water containing 15 glycol ethers at concentrations 0.1-10 mg L-1 is saturated at ambient temperature with NaCl. A carboxen-polydimethylsiloxane-coated fiber is then exposed to the liquid for 20 min and then automatically injected into a capillary GC injection port. Calibration curves were linear for different glycol ethers in the range 0.1-10 mg L-1. Detection limits of each component of the mixture of glycol ethers between 50-500 μg L-1. The SPME method with direct immersion in water results in better sensitivity than methods based on liquid-liquid extraction.

(30) Solid-phase microextraction and gas chromatography-mass spectrometry for determination of monoaromatic hydrocarbons in blood and urine: Application to people exposed to air pollutants, Andreoli_R, Manini_P, Bergamaschi_E, Brustolin_A, Mutti_A, UNIV PARMA, SCH MED, LAB IND TOXCOL, DEPT CLIN MED NEPHROL & HLTH SCI, VIA GRAMSCI 14, I-43100 PARMA, ITALY, UNIV PARMA, SCH MED, LAB IND TOXCOL, DEPT CLIN MED NEPHROL & HLTH SCI, I-43100 PARMA, ITALY, CHROMATOGRAPHIA, 1999, Vol. 50, No. 3-4, pp. 167-172. To assess individual exposure to monoaromatic hydrocarbons (benzene, toluene, ethylbenzene and xylenes BTEX) in biological fluids, a GC-MS method was developed. Headspace sampling of BTEX was by solid-phase microextraction (SPME) with a 75 μm Carboxen-polydimethylsiloxane (PDMS) fiber. Linearity was established for concentrations up to 50 μg L-1. Detection limits, calculated both in human blood and urine, ranged 5-10 ng L-1. Repeatability was in the range 6.5-9.2 % for all compounds. The method was applied to the evaluation of the internal dose of BTEX in a group of cyclists running for 2 h within city routes. Benzene and toluene in blood, and toluene and xylenes in urine significantly increased after exercise as compared to prerun values, such changes being consistent with airborne concentrations. The combination of SPME with GC-MS seems to represent an appropriate analytical approach to detect changes in the concentration of monoaromatic hydrocarbons in biological media resulting from exposure to environmental pollution.
(31) Solid-phase microextraction/capillary gas chromatography for the profiling of confiscated ecstasy and amphetamine, Kongshaug KE, PedersenBjergaard S, Rasmussen KE, Krogh M, UNIV OSLO,SCH PHARM,POB 1068 BLINDERN, N-0316 OSLO, NORWAY UNIV OSLO,SCH PHARM,N-0316 OSLO, NORWAY, CHROMATOGRAPHIA, 1999, Vol.50, No.3-4, pp.247-252 . Impurity profiling of ecstasy and amphetamine seizures was accomplished by solid-phase microextraction (SPME) combined with capillary gas chromatography (GC). Samples were dissolved in 0.1 M aqueous acetate buffer (pH 5.0) as the only manual operation and subsequently subjected to SPME-GC. Ecstasy tablets were analyzed by head-space SPME to avoid contamination of SPME fibers with insoluble tablet components, while illicit amphetamine powders were exposed to immersed SPME. A SPME fiber of polydimethylsiloxane-divinylbenzene was found to provide excellent extraction of both polar and non-polar impurities. For both illicit ecstasy and amphetamine, complex impurity profiles were obtained by SPME providing a high information content. For ecstasy, profiles (relative peak areas) were repeatable within 2.2 to 12.6% RSD (n = 6), while similar data on amphetamine varied between 2.0 and 10.9% RSD (n = 6). No carry-over was observed although each fiber was used for 50 to 100 extractions.

(32) Screening of pesticides from soil samples using solid-phase microextraction, Prosen_H, ZupancicKralj_L, UNIV LJUBLJANA,FAC CHEM & CHEM TECHNOL,ASKERCEVA 5,SLO-1000 LJUBLJANA,SLOVENIA, ACTA CHIMICA SLOVENICA, 1998, Vol.45, No.1, pp.1-18 . Residues of pesticides and their degradation products in soil present a serious problem for crops, soil organisms and humans. For isolation of this type of compounds solid-phase microextraction (SPME) could be used in combination with conventional extraction method. This modern separation method was optimized for extraction of organochlorine and triazine pesticides from soil samples. Analytes were desorbed from the fiber in the injector of a gas chromatograph and determined by either electron capture or mass spectrometric detection. Linearity and limits of detection were tested in the 0.1 - 20.0 ng/g range for organochlorines and 10 - 100 ng/g range for triazines. The method presented could be used for screening of pesticides in contaminated soil samples and offers a simple alternative to established methods of pesticide analysis in soil.

(33) Trends in solid-phase microextraction for determining organic pollutants in environmental samples, Penalver_A, Pocurull_E, Borrull_F, Marce_RM, UNIV ROVIRA & VIRGILI,DEPT QUIM ANALIT & QUIM ORGAN, IMPERIAL TARRACO 1,TARRAGONA 43005,SPAIN UNIV ROVIRA & VIRGILI,DEPT QUIM ANALIT & QUIM ORGAN, TARRAGONA 43005,SPAIN, TRAC-TRENDS IN ANALYTICAL CHEMISTRY, 1999, Vol.18, No.8, pp.557-568 . Solid-phase microextraction (SPME) is a recent technique for sample preparation. It has been used successfully to analyze environmental pollutants in a variety of matrices such as soils, water, and air. SPME is a solvent-free technique which has a number of advantages over more conventional sample preparation techniques such as liquid-liquid extraction (LLE) and solid-phase extraction (SPE). We describe the most recent developments in SPME and some which are being developed, including its coupling to HPLC and CE, the use of new fibers, and the automation of the entire SPME process and its application to field analysis. A summary is given of the most important parameters for applying this extraction technique to the analysis of environmental samples.
(34) Determination of load in blood and urine by SPME/GC, Yu_XM, Yuan_HD, Gorecki_T, Pawliszy_J NA: UNIV WATERLOO, DEPT CHEM, GUELPH WATERLOO CTR GRAD WORK CHEM, WATERLOO, ON N2L 3G1, CANADA, ANALYTICAL CHEMISTRY, 1999, Vol.71, No.15, pp.2998-3002. Lead is the most frequently quantitated toxic metal in biological matrices. In this paper, a method is described for lead determination in whole blood and urine using solid-phase microextraction (SPME) gas chromatography. Lead ion is first derivatized with sodium tetraethylborate to form tetraethyllead, which is then extracted from the headspace over the sample by SPME. The analytical procedure was optimized for coating selection, pH, extraction time, and effect of salt. The relative standard deviation was less than 10% for both urine and blood samples. The limit of detection was 3 and 4 ppb; the limit of quantification is 5 and 10 ppb for urine and blood samples, respectively. Good linearity was found for both urine and blood samples when PDMS coating was used. The standard addition method was used for quantitation. Certified urine and blood samples were analyzed, and good accuracy was obtained.

(35) Analysis of diesel fuel contamination in soils by near-infrared reflectance spectrometry and solid phase microextraction-gas chromatography, Malley_DF, Hunter_KN, Webster_GRB, FISHERIES & OCEANS CANADA, INST FRESHWATER, 501 UNIV CRESCENT, WINNIPEG, MB R3T 2N6, CANADA, PDK PROJECTS INC, WINNIPEG, MB R3T 0E7, CANADA, UNIV MANITOBA, DEPT SOIL SCI, WINNIPEG, MB R3T2N2, CANADA, JOURNAL OF SOIL CONTAMINATION, 1999, Vol.8, No.4, pp.481-489. A feasibility study was undertaken to determine whether the rapid, nondestructive analytical technology near-infrared reflectance spectrometry (NIRS) could be used to predict total petroleum hydrocarbon (TPH) in contaminated soil. Hydrocarbon concentrations were determined on samples of diesel-contaminated soils by the solid phase microextraction-gas chromatography (SPME-GC) method. The same samples were then scanned for near-infrared reflectance spectrometry over the wavelength range 1100 to 2498 nm. Calibrations were developed between the NIR spectral data and the reference SPME-GC chemical data using stepwise multiple linear regression. Linear regression relationships between NIR-predicted TPH concentrations and reference data had r(2) of 0.68 and 0.72. These results indicate that the combination of NIRS and SPME-GC shows promise as a method for rapid estimation of TPH in soil. A major hurdle in the evaluation of methodology for hydrocarbons residues in soil is the challenge posed by the weathering of such residues.

(36) Development of a SPME-GC method for the determination of organic compounds in wastewater, Grote_C, Belau_E, Levens_K, Wunsch_G NA: FRAUNHOFER INST TOXICOL & AEROSOL RES, NIKOLAI FUCHS STR 1, D-30625 HANNOVER, GERMANY, FRAUNHOFER INST TOXICOL & AEROSOL RES, D-30625 HANNOVER, GERMANY, ACTA HYDROCHIMICA ET HYDROBIOLOGICA, 1999, Vol.27, No.4, pp.193-199. IS: 0323-4320 DT: Article AB: A manual SPME method is presented for the analysis of organic compounds in industrial wastewater. 24 compounds commonly found in the wastewater of a chemical plant in northern Germany have been selected as reference compounds. Precision, linearity, and detection limits have been determined. Moreover, the effect of methanol content, pH value, salt content, and an excess of compounds on the extraction process have been studied. Several compounds have been investigated for their applicability as internal standards to quantify the compounds of interest. Since the method will later be
transferred to a fully automated SPME-GC system, which will be operated directly on-site at an industrial wastewater purification plant, special attention has been paid to the analysis of real wastewater samples. In this context, the fibre stability has been studied by performing 53 extraction/desorption cycles from one wastewater sample. Neither a decrease in fibre performance nor in precision has been observed indicating that the proposed method is suitable for the analysis of real wastewater.

(37) Analysis of organochlorine compounds in water by solid phase microextraction and gas chromatography, Zhang_DN, Zhou_ZP, Tang_YZ, Wu_CY, Zhan_W, Xu_Y NA: WUHAN UNIV, DEPT CHEM, WUHAN 430072, PEOPLES R CHINA INST HYDROBIOL, WUHAN 430072, PEOPLES R CHINA, CHINESE JOURNAL OF ANALYTICAL CHEMISTRY, 1999, Vol.27, No.7, pp.768-772. In this work, both, solid phase microextraction (SPME) and solid phase extraction (SPE) were used to enrich organochlorine compounds in water samples and analyzed by gas chromatography with electron capture detector. The operating conditions of SPME have been studied and different kinds of solid phase were compared. Linear alkylene sulfonate (LAS) was added to the samples to investigate its effect on the analysis. The results indicated that polyacrylate was better than other commercial solid phases in extraction of moderated polar organic compounds and the sensitivity of SPME was higher than SPE. LAS affect much in liquid-liquid extraction and headspace SPME; but it has little effect on SPE and direct-SPME method. The applications showed that SPME was a fast and effective method in sample preparation.

(38) Studies on the application of solid-phase microextraction for analysis of volatile organic sulphur compounds in gaseous and liquid samples, Wardencki_W, Namiesnik_J, GDANSK TECH UNIV, FAC CHEM, DEPT ANALYT CHEM, G NARUTOWICZA STR 11-12, PL-80952 GDANSK, POLAND, CHEMIA ANALITYCZNA, 1999, Vol.44, No.3A SIS, pp.485-493. The possibility of application of the solid-phase microextraction (SPME) sampling for quantitative analysis of some volatile organic sulphur compounds (VOS) in both gaseous and aqueous samples was examined. The sorption and desorption time profiles were determined in order to optimize the isolation conditions for VOS from gaseous (nitrogen or propane-buthane mixture) and liquid phases (aqueous solution). The applicability of laboratory-built trap for focusing the tested compounds before introduction them on chromatographic column has been also studied. The obtained results have confirmed the utility of the SPME technique for extraction of VOS from gas samples in the concentration range of 5-100 mg l(-1) and from water of 100 mg l(-1)-5 mg l(-1). For the tested concentration range good linearity between area and concentration was obtained. Furthermore, the working conditions for a flame photometric detector were optimized.

The efficiency of direct solid-phase microextraction (SPME) was determined for 27 selected volatile and semivolatile organic compounds (BTEX, chloro- and bromobenzenes, chlorinated pesticides and PCBs). The fibres used were 7 μm polydimethylsiloxane (PDMS), 30 μm PDMS, 100 μm PDMS, 65 μm PDMS:divinylbenzene, 85 μm m polyacrylate, 65 μm Carbowax- divinylbenzene, 75 μm Carboxen-PDMS and a new 65 μm C8 fibre. Extraction yields for these compounds were calculated under standardised conditions: 75 μm Carboxen-PDMS was found to be the most efficient fibre for compounds with low boiling points. Although 65 μm C8 can be used for extraction of all compounds studied, in no one case is it the most effective coating. 100 μm m PDMS and the more polar coatings can be used for a broad range of compounds, whereas application of 7 μm and 30 μm PDMS cannot be recommended. Interfibre comparison revealed significant differences between three different Carboxen-PDMS fibres. The results enable suitable coatings to be chosen for each of the 27 compounds and for substances with similar properties.

Simultaneous analysis of thiols, sulphides and disulphides in wine aroma by headspace solid-phase microextraction-gas chromatography

Cuticular hydrocarbons correlated with reproductive status in a queenless ant

Reproductive division of labour is regulated behaviourally in social insects lacking morphologically specialized castes. The directional nature of dominance interactions shows that recognition occurs, but little is known about its basis. In the queenless ant Dinoponera quadriceps, the top worker in the hierarchy ('alpha') mates and produces offspring in each colony, while other workers remain virgin. Dominant ants frequently rub one antenna of subordinates against their own cuticle, and alpha and infertile nest-mates consistently differ in their relative proportions of the cuticular hydrocarbon 9- hentriacontene (9-C-31). The second-ranking 'beta' occasionally lays unfertilized eggs and we show that she has less 9-C-31 than the alpha but more than infertile workers. To investigate further the link between 9-C-31 and ovarian activity, we experimentally removed alpha workers.
(n = 11 individuals) and used solid-phase microextraction (SPME) with gas chromatography to measure changes in 9-C-31 on live beta workers which attained alpha status. The proportion of 9-C-31 on the replacement alpha increased significantly after six weeks, in parallel with her gain in fecundity. We discuss whether 9-C-31 provides honest information about egg-laying ability enabling ants to recognize the different classes of nest-mates involved in reproductive conflicts. Such fertility cues could reliably underpin the antagonistic interactions occurring in insect societies.

(43) Recent trends in trace element determination and speciation using inductively coupled plasma mass spectrometry AU: Vanhaecke_F, Moens_L NA: STATE UNIV GHENT,INST NUCL SCI,ANALYT CHEM LAB,PROEFTUNINSTR 86,B-9000 GHENT,BELGIUM JN: FRESENIUS JOURNAL OF ANALYTICAL CHEMISTRY, 1999, Vol.364, No.5, pp.440-451 IS: 0937-0633 DT: Article AB: During the past decade, inductively coupled plasma mass spectrometry (ICPMS) has evolved from a delicate research tool, intended for the well-trained scientist only, into a more robust and well-established analytical technique for trace and ultra-trace element determination, with a few thousand of instruments used worldwide. Despite this immense success, it should be realized that in its 'standard configuration' - i.e. equipped with a pneumatic nebulizer for sample introduction and with a quadrupole filter - ICPMS also shows a number of important limitations and disadvantages: (i) the occurrence of spectral interferences may hamper accurate trace element determination, (ii) solid samples have to be taken into solution prior to analysis and (iii) no information on the 'chemical form' in which an element appears can be obtained. Self-evidently, efforts have been and still are made to overcome the aforementioned limitations to the largest possible extent. The application of a double focusing sector field mass spectrometer in ICPMS instrumentation offers a higher mass resolution, such that spectral overlap can be avoided to an important extent. Additionally, in a sector field instrument, photons are efficiently eliminated from the ion beam, resulting in very low background intensities, making it also very well-suited for extreme trace analysis. Also the combination of the ICP as an ion source and a quadrupole filter operated in a so-called 'alternate' stability region, an ion trap or a Fourier transform ion cyclotron resonance mass spectrometer allows high(er) mass resolution to be obtained. With modern quadrupole-based instruments, important types of spectral interferences can be avoided by working under 'cool plasma' conditions or by applying a collision cell. The use of electrothermal vaporization (ETV) or especially laser ablation (LA) for sample introduction permits direct analysis of solid samples with sufficient accuracy for many purposes. The application range of LA-ICPMS has become very wide and the introduction of UV lasers has led to an improved spatial resolution. Solid sampling ETV-ICPMS on the other hand can be used for some specific applications only, but accurate calibration is more straightforward than with LA-ICPMS. Limited multi-element capabilities, resulting from the transient signals observed with ETV or single shot LA, can be avoided by the use of a time-of-flight (TOF) ICPMS instrument. Finally, when combined with a powerful chromatographic separation technique, an ICP-mass spectrometer can be used as a highly sensitive, element-specific multi-element detector in elemental speciation studies. Especially liquid (HPLC-ICPMS) and - to a lesser extent - gas (GC-ICPMS) chromatography have already been widely used in combination with ICPMS. Speciation work, sample preparation is often observed to be troublesome and this aspect is presently receiving considerable attention. For GC-ICPMS, new sample pretreatment approaches, such as headspace solid phase microextraction (headspace SPME) and the purge-and-trap technique have been
introduced. Also supercritical fluid chromatography (SFC) and capillary electrophoresis (CE) show potential to be of use in combination with ICPMS, but so far the application ranges of SFC-ICPMS and E-ICPMS are rather limited. It is the aim of the present paper to concisely discuss the aforementioned recent 'trends' in ICPMS, using selected real-life applications reported in the literature.

(44) Determination of polychlorinated biphenyls in human blood serum by SPME AU: Poon_KF, Lam_PK, Lam_MHW NA: CITY UNIV HONG KONG, DEPT BIOL & CHEM, CTR COASTAL POLLUT & CONSERVAT, TAT CHEE AVE, KOWLOON, HONG KONG CITY UNIV HONG KONG, DEPT BIOL & CHEM, CTR COASTAL POLLUT & CONSERVAT, KOWLOON, HONG KONG JN: CHEMOSPHERE, 1999, Vol.39, No.6, pp.905-912 IS: 0045-6535 DT: Article AB: We report a direct immersion SPME - GC/mu ECD method for the determination of non-volatile pollutants (Aroclor 1254) in human blood plasma using an enzymatic proteolytic approach to overcome the protein fouling problem. A nonspecific serine protease, Proteinase K, is used to remove the fouling interference. Significant improvement in relative repeatability from 28.9% to 3.4% (n=10) was obtained. Analyte recovery up to 93% and detection limit of 1.0 ppb (total PCB) were achieved.

(45) Determination of menthol and menthone in food and pharmaceutical products by solid-phase microextraction-gas chromatography AU: Ligor_M, Buszewski_B NA: NICHOLAS COPERNICUS UNIV, FAC CHEM, DEPT ENVIRONM CHEM & ECOANALYT, GAGARIN ST 7, PL-87100 TORUN, POLAND NICHOLAS COPERNICUS UNIV, FAC CHEM, DEPT ENVIRONM CHEM & ECOANALYT, PL-87100 TORUN, POLAND JN: JOURNAL OF CHROMATOGRAPHY A, 1999, Vol.847, No.1-2, pp.161-169 IS: 0021-9673 DT: Article AB: In the current contribution the optimization of menthol and menthone isolated from food and pharmaceutical samples by solid-phase microextraction (SPME) will be presented. Extraction efficiencies for commercial (polydimethylsiloxane) and laboratory-made imethylsiloxane) coated quartz fibers were compared. The results show, that SPME coupled with GC-flame ionisation detection is a reproducible method for isolation and for qualitative and quantitative determination of menthol and menthone at ppm as well as ppb levels. The described procedure can be recommended for routine food and pharmaceutical analyses.

(46) Solid phase microextraction (SPME) analysis of whole air samples AU: Chai_M, Tang_YZ NA: CONOR PACIFIC ENVIRONM, 2 TIPPET RD, TORONTO, ON M3H 2V2, CANADA CONOR PACIFIC ENVIRONM, TORONTO, ON M3H 2V2, CANADA JN: INTERNATIONAL JOURNAL OF ENVIRONMENTAL ANALYTICAL CHEMISTRY, 1998, Vol.72, No.1, pp.77-82 IS: 0306-7319 DT: Article AB: Air samples can be collected by a number of means and whole air sample collection in canisters or bags is one of the most frequently used options. However, whole air samples normally require preconcentration before analysis to achieve sufficient method sensitivity for trace components and the procedures are usually time consuming. This application note demonstrates that such a preconcentration for whole air samples can be done quickly with the solid phase microextraction (SPME) technique, which is fast, simple to use, low in cost, solvent free, and combines the sample concentration and introduction procedures for whole air samples into one single step. In addition to the improved sensitivity, the SPME also provides a better precision than direct injection of
an air sample with a syringe. WA: solid phase microextraction, whole air samples, preconcentration, VOCs, GC

(47) GC trace analysis of haloethers in water - Comparison of different extraction techniques AU: Wennrich_L, Engwald_W, Popp_P NA: UNIV LEIPZIG, INST ANALYT CHEM, LINNESTR 3, D-04103 LEIPZIG, GERMANY UNIV LEIPZIG, INST ANALYT CHEM, D-04103 LEIPZIG, GERMANY CTR ENVIRONM RES LTD, DEPT ANALYT CHEM, D-04318 LEIPZIG, GERMANY JN: INTERNATIONAL JOURNAL OF ENVIRONMENTAL ANALYTICAL CHEMISTRY, 1999, Vol.73, No.1, pp.31-41 IS: 0306-7319 DT: Article AB: The capabilities of three extraction techniques (solid-phase microextraction, solid-phase extraction, and liquid-liquid extraction) for the GC trace analysis of di- and tetrachlorinated haloethers in natural water samples were studied. The extraction procedures are described and evaluated with respect to recoveries, precision and detection limits using FID and MS detection. The results are compared. Investigations of the matrix influence show that efficiency and precision of the extraction procedures tested are not significantly influenced by dissolved organic matter in the relevant concentration range. Combined with CC-MS in SIM mode all three extraction techniques are generally suitable for the haloether analysis at ng/L level. However, the precision of solid-phase microextraction (SPME) is poor in this concentration range. Nevertheless, because of several advantages (low time consuming for sample preparation, no employment of solvents) the SPME is favorable for the determination of haloethers at μg/L level, like in Elbe river water samples.

(48) Evaluation of solid-phase microextraction for sampling of volatile organic sulfur compounds in air for subsequent gas chromatographic analysis with atomic emission detection AU: HaberhauerTroyer_C, Rosenberg_E, Grasserbauer_M NA: VIENNA UNIV TECHNOL, INST ANALYT CHEM, GETREIDEMARKT 9-151, A-1060 VIENNA, AUSTRIA UNIV TECHNOL, INST ANALYT CHEM, A-1060 VIENNA, AUSTRIA JN: JOURNAL OF CHROMATOGRAPHY A, 1999, Vol.848, No.1-2, pp.305-315 IS: 0021-9673 DT: Article AB: The use of solid-phase microextraction (SPME) followed by GC-AED (atomic emission detection) for the analysis of volatile organic sulfur compounds (methanethiol, dimethyl sulfide, isopropanethiol and isobutanethiol) in spiked air samples was investigated. Gaseous standard mixtures were generated by means of a permeation apparatus with stopped flow facilities to permit sampling of the analytes with the SPME fiber. Detection limits between 4 ppt for dimethyl sulfide and isobutanethiol and 50 ppt (v/v) for methanethiol were achieved for extraction with the Carboxen-PDMS (polydimethylsiloxane) fiber followed by GC-AED analysis. The comparison of the performance of the 100 μm PDMS and the 75 μm Carboxen-PDMS fiber coating demonstrates the superiority of the latter in terms of sensitivity and repeatability. Despite the principal applicability of SPME to sampling of organosulfur compounds, artifacts are observed during analysis. Furthermore, the low storage stability, the dependence of the extraction efficiency on the relative humidity and the pronounced differences in sensitivity between fibers limit the usefulness of the method for quantitative on-site analysis.

procedure extracts aromatic compounds in water at part-per-billion concentrations from aqueous samples using a small disk of poly (dimethyl siloxane) (PDMS) and ultraviolet absorption spectroscopy. The reversed-phase disk (PDMS) removes nonpolar aromatic compounds from contaminated water at equilibrium time measured using standards from each aromatic compound studied. It was found that equilibrium is established in the range of 40-60 min, with the exception of naphthalene and 1-methyl naphthalene, equilibrated within 90 and 100 min, respectively. After the equilibrium is established the concentration of aromatic hydrocarbon in the sorbent disk is determined quantitatively by UV absorption spectra at 260 nm. The detection limit of the procedure was ranging from 0.5 to 10 ppb. Relative standard deviation from the complete procedure was ranging from 3 to 12%. KP: RAMAN-SPECTROSCOPY (50) Studies on the application of solid-phase microextraction for analysis of volatile organic sulphur compounds in gaseous and liquid samples AU: Wardencki_W, Namiesnik_J NA: GDANSK TECH UNIV,FAC CHEM,DEPT ANALYT CHEM,G NARUTOWICZA STR 11-12,PL-80952 GDANSK,POLAND JN: CHEMIA ANALITYCZNA, 1999, Vol.44, No.3, pp.485-493 IS: 0009-2223 DT: Article AB: The possibility of application of the solid-phase microextraction (SPME) sampling for quantitative analysis of some volatile organic sulphur compounds (VOS) in both gaseous and aqueous samples was examined. The sorption and desorption-- time profiles were determined in order to optimize the isolation conditions for VOS from gaseous (nitrogen or propane- buthane mixture) and liquid phases (aqueous solution). The applicability of laboratory-built trap for focusing the tested compounds before introduction them on chromatographic column has been also studied. The obtained results have confirmed the utility of the SPME technique for extraction of VOS from gas samples in the concentration-range of 5-100 mg l(-1) and from water of 100 mg l(-1)-5 mg l(-1). For the tested concentration range good linearity between area and concentration was obtained. Furthermore, the working conditions for a flame photometric detector were optimized.

(51) Analytical characterization of impurities or byproducts in new energetic materials AU: Bunte_G, Pontius_H, Kaiser_M NA: FRAUNHOFER INST CHEM TECHNOL ICT,D-76327 BERGHAUSEN,GERMANY WIWEB,AUSSENSTELLE SWISTTAL HEIMERZHEIM,D-53913 SWISTTAL,GERMANY JN: PROPELLANTS EXPLOSIVES YROTECHNICS, 1999, Vol.24, No.3, pp.149-155 IS: 0721-3115 DT: Article AB: In the last years several new explosives have recently attracted attention as possible alternatives, e.g. for the nitramines RDX and HMX. Hexanitrohexaazaisowurtzitane (HNIW) also known as Cl, 20 is one of them. Objective of the study was to analyse three different Cl 20 samples from different suppliers (E-CL 20 from Thiokol, USA and epsilon- and beta-CL 20 from SNPE, France) with chromatographic and spectroscopic techniques to characterize the chemical and polymorph purity of the materials in order to compare the different samples to each other. From IR-spectroscopic measurements it was determined that all three materials have polymorph purities >95%. To get informations about the chemical purity and possible byproducts or residual solvents the samples were analysed by HPLC, NMR and GC-MSD. For the last a new technique, the so called Solid Phase Micro Extraction, SPME was applied for sample preparation. The chemical purity estimated by HPLC analysis was for all CL 20 samples > 96% while the E-charge of SNPE had the highest purity (98.3%). From NMR-measurements an acetyl- or formyl-substituted byproduct was identified. From NMR as well as from GC-MSD analyses residual amounts of organic solvents have been detected (ethanol or tetrahydrofuran).
Furthermore different spare amounts of other organic components were identified after SPME-treatment and characterization with GC-MSD.

(49) A systematic approach to optimize solid-phase microextraction. Determination of pesticides in ethanol water mixtures used as food simulants AU: Batlle_R, Sanchez_C, Nerin_C NA: UNIV ZARAGOZA,CTR POLITECN SUPER,DEPT ANALYT CHEM,C MARIA DE LUNA 3,E-50015 ZARAGOZA,SPAIN UNIV ZARAGOZA,CTR POLITECN SUPER,DEPT ANALYT CHEM,E-50015 ZARAGOZA,SPAIN JN: ANALYTICAL CHEMISTRY, 1999, Vol.71, No.13, pp.2417-2422 IS: 0003-2700 DT: Article AB: The optimization of solid-phase microextraction (SPME) of several organochlorine and organophosphorus pesticides is presented, and the influence of variables is discussed. The optimized method is applied to several selected ethanol/water mixtures used as food simulants, and the influence of the ethanol content on the SPME performance is also discussed. Detection limits ranging from 0.02 to 0.04 ng/g for water simulant and from 38.7 to 205.5 ng/g for 95% ethanol simulant were obtained. The relative standard deviation (% RSD) was <20% in all cases. The optimized method is compared with classical liquid-liquid extraction (LLE).

(50) Evaluating peats for their capacities to remove odorous compounds from liquid swine manure using head space "solid- phase microextraction" AU: Rizzuti_AM, Cohen_AD, Hunt_PG, Vanotti_MB NA: UNIV S CAROLINA,DEPT GEOL SCI,COLUMBIA,SC,29208 USDA ARS,COASTAL PLAINS SOIL WATER & PLANT RES R,FLORENCE,SC,29501 JN: JOURNAL OF ENVIRONMENTAL SCIENCE AND HEALTH PART B-PESTICIDES FOOD CONTAMINANTS AND AGRICULTURAL WASTES, 1999,Vol.34, No.4, pp.709-748 IS: 0360-1234 DT: Article AB: This paper reports on research designed to investigate the capacities of different highly characterized peats to remove odorous compounds from liquid swine manure (LSM). Peat types representing a wide range of properties were tested in order to establish which chemical and physical properties might be most indicative of their capacities to remediate odors produced by LSM. Eight percent slurries (of peat/LSM) were measured for odor changes after 24 hours using odor panel and GC/MS-Solid-phase microextraction (GC/MS-SPME) analysis. The GC/MS-SPME and odor panel results indicated that, although all peats tested in this study were found to be effective at removing odor-causing compounds found in LSM, some peats tended to work better than others. Overall, the peats that were the most effective at removing odor-causing compounds tended to have lower bulk densities, ash contents, fulvic acids contents, and guaiacyl lignins contents, and higher water holding capacities, hydraulic conductivities, "total other lignins" contents, hydrogen contents, carbon contents, and total cellulose contents. GC/MS-SPME analysis was found to be a reasonably inexpensive and efficient way of conducting this type of research. It allows one to identify a large number of the odor-causing compounds found in LSM, and more importantly, to detect with some precision specific differences in the amounts of these compounds between peat types.

(51) Optimization of solid-phase microextraction conditions using a response surface methodology to determine organochlorine pesticides in water by gas chromatography and electron-capture detection AU: Aguilar_C, Penalver_A, Pocurull_E, Ferre_J, Borrell_F, Marce_RM NA: UNIV ROVIRA & VIRGILI,DEPT QUIM ANALIT & QUIM ORGAN,IMPERIAL TARRACO 1,TARRAGONA 43005,SPAIN UNIV
A response surface methodology was applied to optimise the solid-phase microextraction (SPME) conditions using a polyacrylate-coated fiber to determine thirteen organochlorine pesticides from water. Analyses were performed using gas chromatography-electron-capture detection. Variables affecting absorption in both the headspace and immersion extraction were optimised by using a response surface generated with a Doehlert design, and the results were compared. The immersion SPME method was selected since higher recoveries were obtained for most of the compounds studied. The method developed was applied to the analysis of tap and Ebro river water samples. The linear range of most pesticides for real samples was found to be between 0.001 and 2.5 \mu g l^{-1} and the limits of detection were between 0.15 and 0.35 ng l^{-1}. The repeatability and the reproducibility between days of the method (n=6), expressed as relative standard deviation, for tap water spiked at a level of 1 ng l^{-1} were between 5.7 and 25.6% and between 7.6 and 26.5%, respectively.

Identification of a new blend of apple volatiles attractive to the apple maggot, Rhagoletis pomonella

A new blend of volatiles from apples was identified as the key attractants for the apple maggot BS' Rhagoletis pomonella (Walsh). The new five-component blend contains butyl butanoate (10%), propyl hexanoate (4%), butyl hexanoate (37%), hexyl butanoate (44%), and pentyl hexanoate (5%) compared with a previously reported seven-component mix of hexyl acetate (35%), (E)-2-hexen-1-yl acetate (2%), butyl 2-methylbutanoate (8%), propyl hexanoate (12%), hexyl propanoate (5%), butyl hexanoate (28%), and hexyl butanoate (10%). Volatiles from five different varieties of apple elicited reproducible and high EAD responses from R. pomonella antennae to the same five chemicals. In flight-tunnel choice tests involving red sticky spheres with odor sources, the new five-component blend of apple volatiles showed significantly more activity than the previous seven-component blend or the single compound, butyl hexanoate. In a field trial catches with the new five-component blend were better than with butyl hexanoate, which is currently used with commercial apple maggot monitoring spheres.

Influence of extraction parameters and medium on efficiency of solid-phase microextraction sampling in analysis of aliphatic aldehydes

The main sorption conditions were optimized in the solid-phase microextraction (SPME) analysis of aldehydes that have different degrees of saturation. Aliphatic aldehydes were analyzed quantitatively in oil matrix and in aqueous solution by GC-MS using SPME sampling. The effectiveness of the immersion and the headspace techniques was compared in water. Samples were analyzed by gas chromatography with mass spectral detection using a medium polar CP WAX 52 CB column. The optimal exposure time was 30 min at 40 degrees C using a
100 µm poly(dimethylsiloxane) coating. A ratio of liquid to headspace volume of 1:1 resulted in the best extraction in headspace analysis. Principal component analysis (PCA) was carried out to find similarities among various aldehydes and among conditions of optimization. The PCA identifies three clusters corresponding to analysis conditions (immersion in water, headspace above water and headspace above oil). The aldehydes behave similarly with the exception of dienals.

(57) Interaction between natural organic matter (NOM) and polycyclic aromatic compounds (PAC) - comparison of fluorescence quenching and solid phase micro extraction (SPME). Doll_TE, Frimmel_FH, Kumke_MU, Ohlenbusch_G, UNIV KARLSRUHE,DIV WATER CHEM,ENGLER BUNTE INST,ENGLER BUNTE RING 1,D-76131 KARLSRUHE,GERMANY UNIV KARLSRUHE,DIV WATER CHEM,ENGLER BUNTE INST,D-76131 KARLSRUHE,GERMANY JN: FRESENIUS JOURNAL OF ANALYTICAL CHEMISTRY, 1999, Vol.364, No.4, pp.313-319. The interaction of phenanthrene and 9-aminophenanthrene with natural organic matter (NOM) of different origin was investigated using the fluorescence quenching approach and the solid phase micro extraction method. The results of both methods are compared in terms of the influence of the concentration of the polycyclic aromatic compounds (PAC) as well as the concentration of the NOM on the observed binding constant. Due to the combination of steady-state and time-resolved fluorescence techniques it could be concluded that the observed fluorescence quenching was caused by a static interaction like a complex formation. While for phenanthrene both analytical methods showed no long term effects and the reaction equilibrium between NOM and phenanthrene was established within the first hour, for 9-aminophenanthrene a slow reaction kinetics (within days) was found indicating specific interactions between NOM and the amino group.

(58) Determination of trace xylene in contaminated palm oil by solid phase micro-extraction and capillary gas chromatography. LA: Chinese, Chen_WR, Guo_CC, Hu_GC, NATL IMPORT FOOD HYG SUPERVIS & INSPECT CTR CHINA, GUANGZHOU 510405,PEOPLES R CHINA JN: CHINESE JOURNAL OF ANALYTICAL CHEMISTRY, 1999, Vol.27, No.6, pp.676-678. Solid phase micro-extraction (SPME) was used to concentrate trace toluene and xylene in a batch of contaminated imported palm oil. The sample was put in a bottle sealed with rubber septum and kept at 60 degrees C in water-bath, an SPME apparatus was injected in head-space of the bottle, equilibrated for one minute, where the volatile organic analytes were-adsorbed by: the SPME fiber, then introduced into the gas chromatographic injector directly. Benzene was used as internal standard and bean oil as simulated matrix to make calibration curves, which were linear in the range of 0.2 similar to 20 mg/kg. The RSD wer in the range of 2.3% similar to 5.3%, the detection limit of toluene and xylene in palm oil was 0.05 mg/kg and 0.6 mg/kg respectively. WA: solid-phase micro-extraction, xylene, palm oil, capillary gas chromatography.

(59) Identification and quantitation of halogenated solvents after solid phase microextraction (SPME). Applications in clinical toxicology, Humbert_L, Dehon_B, Decaestecker_B, Mathieu_D, Houdret_N, Lhermitte_M NA: CHRU LILLE,HOP CALMETTE,LAB BIOCHIM & BIOL MOL,UNITE FONCT TOXICOL,AVE PR J LECLERCQ,F-59037 LILLE,FRANCE, ACTA CLINICA BELGICA, 1999, No.S1, pp.89-93. A simple method for the research and the identification of chlorinated solvents in biological fluids and tissues is described. The solvents are extracted using
headspace solid-phase microextraction and detected or measured by gas chromatography with electron capture detector. Three accidental poisonings are reported: one with carbon tetrachloride, one with trichlorethylene and the last one is a double intoxication with tetrachloroethylene and trichlorethylene.

(60) Selective determination of Se4+ and Se6+ using SPME and GC MS, Guidotti_M, Ravaioi_G, Vitali_M, PRESIDIO MULTIZONALE PREVENZ RIEIITA VIA SALARIA AQUILA 8-I-02100 RIEIITA ITALY UNIV ROMA LA SAPIENZA, IST IGIENE, CATTEDRA IGIENE AMBIENTALE, I- 00100 ROME ITALY, HRC-JOURNAL OF HIGH RESOLUTION CHROMATOGRAPHY, 1999, Vol.22, No.7, pp.414-416. A method for the selective determination of Se4+ and Se6+ using solid phase microextraction (SPME) and GC/MS analysis is presented. Se4+ is selectively derivatized by reaction with 4,5-dichloro-1,2-phenylenediamine to form the corresponding piazselenolo complex, extracted by the SPME fiber, and determined by GC/MS. The RSD at a 5 μg/L concentration was 9.88% and the theoretical detection limit 6 ng/L. The method was employed to test real matrices; tap and river water were analyzed before and after spiking giving a recovery rate of 102% in river mater and 97% in tap water.


(62) Headspace solid-phase microextraction for the determination of polychlorinated biphenyls in soils and sediments, Llompart_M, Li_K, Fingas_M, UNIV SANTIAGO DE COMPOSTELA, FAC QUIM, DEPT QUIM ANALIT NUTR & BROMATOL, E-15706 SANTIAGO COMPOSTALE, SPAIN ENVIRONM CANADA, ENVIRONM TECHNOL CTR, EMERGENCIES SCI DIV, OTTAWA, ON K1A 0H3, CANADA, JOURNAL OF MICROCOLUMN SEPARATIONS, 1999, Vol.11, No.6, pp.397-402. A headspace solid-phase microextraction (HSSPME) method has been developed for the quantification of polychlorinated biphenyls (PCBs) in soils and sediments. In this study polydimethylsiloxane fibers with a 100 μm thickness were used. Parameters affecting the extension of the adsorption process were studied (sampling time, sample size, volume of water and acetone added to the sample, volume of headspace, and extraction temperature). Because the time for reaching equilibrium between phases takes several hours, it was necessary to work in nonequilibrium conditions to keep the sample analysis to a reasonable time. Soil and sediment samples were weighed in a glass vial and, after the addition of 1 ml of water and a stirring magnetic bar, the vial was closed and heated to 100 degrees C. The sample was stirred and the SPME fiber was exposed to the headspace over the soil-water slurry for 30 min. Finally, the fiber was inserted in the gas chromatograph (GC) injector port and GC-mass selective detector analysis was carried out. The proposed HSSPME method exhibits excellent linearity, sensitivity, and precision. The detection limit was in the subnanogram per gram level, and repeatability tests showed a relative standard deviation below 10%. This method has been applied to two real contaminated sediments. In these real samples, standard addition calibrations were done and the concentrations of PCBs found with the proposed method were in good agreement with the certified PCB values.
Sol-gel method for the preparation of solid-phase microextraction fibers, Zhou_ZP, Wang_ZY, Wu_CY, Zhan_W, Xu_Y, WUHAN UNIV, DEPT CHEM, WUHAN 430072, PEOPLE'S R CHINA; CHINESE ACAD SCI, INST HYDROBIOL, WUHAN 430072, PEOPLE'S R CHINA; ANALYTICAL LETTERS, 1999, Vol. 32, No. 8, pp. 1675-1681. A novel sol-gel method is applied for the preparation of solid-phase microextraction (SPME) fibers. Scanning electron microscopy experiments suggested a porous structure for the poly(dimethylsiloxane) (PDMS) coating. SPME-GC analysis provided evidence that the sol-gel fibers have some advantages, such as high thermal stability, efficient extraction rates, high velocities of mass transfer, and spacious range of application. WA: solid-phase microextraction, sol-gel method, gas chromatography, solid-phase coating

Comparison of catechins and aromas among different green teas using HPLC/SPME-GC, Baptista_JAB, Tavares_JFD, Carvalho_RCB, UNIV Acores, DEPT CIENCIAS TECNOL & DESENVOLVIMENTO, RUA MAE DEUS, P-9502 SAO MIGUEL, Acores, PORTUGAL; CTR SAUDE, DIRRECAO REG SAUDE PONTA DELGADA, SAO MIGUEL, Acores, Portugal; FOOD RESEARCH INTERNATIONAL, 1998, Vol. 31, No. 10, pp. 729-736. Green tea polyphenols (GTP) from Camellia sinensis (L.) O. Kuntze are the major water soluble components in tea liquor. The GTP extraction yield was determined using different extraction times from 10 to 60 min at 70 degrees C, and also at different temperatures from 50 degrees C to 100 degrees C, keeping the extraction time constant. The composition of the GTP (catechins) from samples of different origins was determined by RP-HPLC, measuring the absorbance at 280 nm. The calibration curves of the catechins were linear between 5 ng and 2 mu g, and their C.V. values for the quantitation were less than 4.0% for four replicates using four different sets of each type. The total epicatechin derivatives (EPD) and epigallocatechin-3-gallate (EGCG) from Azorean green tea, accounted for 74.5 and 47.9% (w/w) of the total GTP, respectively, and were compared with that from tea samples of different origins. The EGCG:caffeine ratio in Azorean green tea was fourfold higher as compared with others, which suggested a good source of a chemopreventive agent. The aroma composition of different green tea samples was compared using the SPME/GC headspace methodology.

An attempt by solid-phase microextraction with on-column silylation for a rapid and highly sensitive determination of bisphenol A, Takao_Y, Lee_HC, Arizono_K NA: NAGASAKI UNIV, FAC ENVIRONM STUDIES, 1-14 BUNKYO MACHI, NAGASAKI 8528521, JAPAN; PREFECTURAL UNIV KUMAMOTO, FAC ENVIRONM & SYMBIOT SCI, KUMAMOTO 8628502, JAPAN; BUNSEKI KAGAKU, 1999, Vol. 48, No. 6, pp. 589-593. A combination solid-phase microextraction (SPME) and on-column silylation was applied for a rapid and highly sensitive determination of environmental endocrine disrupters in water samples. In this study, bisphenol A (BPA, 2,2-bis (4-hydroxyphenyl) propane) was selected. BPA was extracted by absorption over the surface of SPME cider which was directly exposed to the sample. The fiber was introduced into the injection port of GC/MS, where BPA was thermally desorbed followed by injecting bis(trimethylsilyl)trifluoroacetamide (BSTFA) as a derivative with a syringe in the gas phase under He flow. In a comparison without silylation, the peak area of on-column silylated BPA was increased to approximately 20 times. The detection limit was about 1 ppb, lower than expected for originating in a epoxy-resin adhesive from a SPME fiber.
Volatiles from Fusarium verticillioides (Sacc.) Nirenb, and their attractiveness to nitidulid beetles, Bartelt_RJ, Wicklow_DT, ARS, BIOACT AGENTS RES UNIT, NATL CTR AGR UTILIZAT RES, USDA, 1815 N UNIV ST, PEORIA, IL 61604, JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY, 1999, Vol. 47, No. 6, pp. 2447-2454. It is known that sap beetles (Coleoptera: Nitidulidae) can vector the fungus Fusarium verticillioides (Sacc.) Nirenb. (= F. moniliforme Sheldon), which causes an important ear-rot disease in corn and also produces fumonisin mycotoxins. The volatiles produced by this fungus were studied to establish whether they could attract sap beetles. Such an association would suggest more than just an incidental role in transmission of the fungus by the beetles. F. verticillioides consistently produces a blend of five alcohols (ethanol, 1-propanol, 2-methyl-1-propanol, 3-methyl-1-butanol, and 2-methyl-1-butanol), acetaldehyde, and ethyl acetate. Ethanol is the most abundant alcohol. The fungus also produces four phenolic compounds (the most abundant of which is ethylguaiacol), a series of presently unidentified sesquiterpene hydrocarbons, and an unidentified compound that is probably a 10-carbon ketone. Solid-phase microextraction was the key technique used in volatile analysis. The volatile profiles change over time and differ somewhat among fungal strains: The alcohols, aldehyde, and ester always appeared first and were present far each strain. Production of the phenolics lagged by several days; and in some strains these compounds were barely detectable. Volatile production eventually diminished in all strains. All strains were attractive to the sap beetle, Carpophilus humeralis (F.), in wind-tunnel bioassays. Attraction was correlated primarily to the presence of the alcohols, acetaldehyde, and ethyl acetate, rather than to the phenolics. To verify that the identified culture volatiles were responsible for beetle attraction, cultures were quantitatively simulated with synthetic chemicals, and the cultures and corresponding synthetic mixtures were then compared by bioassay. The comparisons were favorable. Volatile emission patterns from cultures were fairly robust with respect to inoculum level or incubation temperature, but some manipulation was possible. For example, after freeze-drying and rehydrating (a rapid simulation of winter/spring conditions), F. verticillioides produced ethyl acetate and other esters at unusually high levels. The fungus produced attractive volatiles following ear inoculation of milk-stage field corn as well as on sterile, mature kernels in the laboratory.

Improvement of the chemometric variety characterization of wines by improving the detection limit for aroma compounds, Weber_J, Beeg_M, Bartzsch_C, Feller_KH, Garcia_DD, Reichenbacher_M, Danzer_K, FACHHSCH JENA, FACHBEREICH MATH, TATZENDPROMENADE 1B, D-07745 JENA, GERMANY, FACHHSCH JENA, FACHBEREICH MATH, D-07745 JENA, GERMANY, UNIV JENA, INST ANORGAN & ANALYT CHEM, D-6900 JENA, GERMANY, HRC-JOURNAL OF HIGH RESOLUTION CHROMATOGRAPHY, 1999, Vol. 22, No. 6, pp. 322-326. Headspace-SPME followed by capillary gas chromatography/mass spectrometry was used to investigate 90 German wines originating from different grape varieties, vintages, and growing areas. Aromagrams obtained in single ion monitoring (SIM) and in the full scan detection mode (SCAN) of quadrupole mass spectrometer were compared. Detection limits, reproducibility, and linearity for some aroma relevant substances were estimated over a wide concentration range. The advantages of SIM, data set (lower detection limit, better reproducibility and linearity in the smaller concentration ranges) should be reflected in more reliable results in classification of wines. To verify these expectation, classification of variety by discriminant analysis was
performed with cross validation using both SIM and SCAN data sets including 19 aroma compounds, respectively.

(68) Examination of aroma production kinetics of different commercial wine yeasts in fermenting Muscat Ottonel wines with the help of SPME head-space sampling and fast GC analysis, Vas_G, Blechschmidt_I, Kovacs_T, Vekey_K NA: MINIST AGR, RES INST VITICULTURE & ENOL, POB 83, H-3301 EGER, KOLYUKTETO, HUNGARY, ACTA ALIMENTARIA, 1999, Vol.28, No.2, pp.133-140. Solid phase microextraction (SPME) coupled to fast capillary gas chromatography was used for monitoring the wine fermentation process. This combination offers a simple, quick and sensitive approach suitable for characterization of head-space components of wines during the fermentation process without a complicated sample preparation procedure. In this work this method was used to observe the differences in aroma production between three different commercial yeasts and the indigenous yeast flora.

(69) Determination of volatiles from red wines made by carbonic maceration using solid phase microextraction (SPME) technique, Vas_G, Lorincz_G NA: RES INST VITICULTURE & ENOL, POB 83, H-3300 EGER, HUNGARY, ACTA ALIMENTARIA, 1999, Vol.28, No.1, pp.95-101 . Article AB: A winemaking technology termed "maceration carbonique" (MC), affecting the volatile components, was examined. Solid Phase Microextraction sample preparation and GC technique were used to examine the volatile components of the wines. The wines made by carbonic maceration had higher quantity of diethyl succinate and ethyl lactate, but lower methanol and hexanol contents than the skin-fermented wine.

(70) Occurrence and distribution of organic contaminants in the aquatic system in Berlin. Part III: Determination of synthetic musks in Berlin surface water applying solid-phase microextraction (SPME) and gas chromatography-mass spectrometry (GC-MS), Heberer_T, Gramer_S, Stan_HJ, TECH UNIV BERLIN, INST FOOD CHEM, GUSTAV MEYER ALLEE 25, D-13355 BERLIN, GERMANY JN: ACTA HYDROCHIMICA ET HYDROBIOLOGICA, 1999, Vol.27, No.3, pp.150-156 . Polycyclic musks and nitro musks were found as environmental pollutants in screening analyses of 30 representative surface water samples collected from rivers, lakes, and canals in Berlin. These synthetic musks, which are used as fragrances in cosmetics, detergents, and other products, are discharged by the municipal sewage treatment plants into Berlin's surface waters. In particular, the polycyclic musks 1,3,4,6,7,8- hexahydro-4,6,6,7,8,8-hexamethylocyclopenta-(g)- 2-benzopyrane (HHCB; Galaxolide(R), Abbalide(R)) and 7-acetyl-1,1,3,4,4,6- hexamethytraline (AHTN; Tonalide(R), Fixolide(R)) were found in the receiving surface waters at considerable concentrations up to the mu g/L-level. In the Wuhle, a small brook almost totally consisting of sewage effluents? maximum concentrations were 12.5 mu g/L for HHCB and 6.8 mu g/L for AHTN. Additionally, the polycyclic musk 4-acetyl-1,1,1-dimethyl-6-tert- butylindane (ADBI; Celestolide(R), Crysolide(R)) and 1-tert- butyl-3,5-dimethyl-2,6-dinitro-4-acetylbenzene (musk ketone) were detected at low concentrations in most of the samples. Two other nitro musks, namely 1,1,3,5-pentamethyl-4,6- dinitroindene (musk moskene) and 1-tert-butyl-3,5-dimethyl-2,4,6-trinitrobenzene (musk xylene), were only detected in a single surface water sample. Solid-phase microextraction (SPME) with detection by gas chromatography-mass spectrometry (GC-MS) has proven to be a rapid and reliable tool for the screening of synthetic musks in surface and
sewage water samples. Internal calibration with a suitable internal standard enables reproducible quantitation of the analytes down to the low ng/L-level.

(71) On calibration of solid phase microextraction-gas chromatography-mass spectrometry system for analysis of organic air contaminants using gaseous standard mixtures, Namiesnik_J, Gorlo_D, Wolska_L, Zygmunt_B, GDANSK TECH UNIV,FAC CHEM,DEPT ANALYT CHEM,11-12 G NARUTOWICZA ST,PL-80952 GDANSK,POLAND, CHEMIA ANALITYCZNA, 1999, Vol.44, No.2, pp.201-213. The paper briefly touches the general problems related to calibration in analytical measurements. The special requirements with respect to calibration in methods of air organic contaminants determination (those based on solid phase microextraction, SPME) are stressed. A convenient apparatus for generation of gaseous mixture with low organic analyte content with facilities for SPME sampling is described. The procedure for temperature and humidity corrected calibration is proposed and studies on effects of these parameters on calibration curves are presented.

(72) Study of TEX (toluene, ethylbenzene, xylenes) scavenging by raindrops, Ferronato_C, Kaluzny_P, Jacob_V, Laffond_M, Foster_P, GRECA,39 BLVD GAMBIETTA,F-38000 GRENOBLE,FRANCE, FRESNIUS ENVIRONMENTAL BULLETIN, 1998, Vol.7, No.3A-4A SISI, pp.246-253 . Rainwater samples were collected in Grenoble during 1993-1995. Concentration measurements of toluene, ethylbenzene, m-xylene and o-xylene have been carried out concurrently in the gas phase and in the rainwater during precipitation events. Results obtained suggest that TEX scavenging is predominant at low temperature and during low rain intensity precipitation.

(73) Electrochemical control of solid phase micro-extraction using unique conducting polymer coated fibers, Gbatu_TP, Ceylan_O, Sutton_KL, Rubinson_JF, Galal_A, Caruso_JA, Mark HB, UNIV CINCINNATI,DEPT CHEM,POB 210172,CINCINNATI,OH,45221 UNITED ARAB EMIRATES UNIV,FAC SCI,DEPT CHEM,AL AIN,U ARAB EMIRATES, ANALYTICAL COMMUNICATIONS, 1999, Vol.36, No.5, pp.203-205 . The use of a solid phase micro-extraction (SPME) method with poly(3-methylthiophene) coated platinum micro-fiber electrodes to extract arsenate ions from aqueous solutions without derivatization is described. The fibers were fabricated by cycling the working electrode between -0.20 and +1.7 V (vs. Ag/AgCl) in an acetonitrile solution containing 50 mM 3- methylthiophene monomer and 75 mM tetrabutylammonium tetrafluoroborate (TBATFB) electrolyte. All electrochemical procedures (extraction and expulsion) were conducted in a three-electrode system. After fabrication, the conducting polymer film was immersed in the sample solution and converted to its oxidized, positively charged form by applying a constant potential of +1.2 V with respect to Ag/AgCl reference electrode. Arsenate ions migrated into the film to maintain electroneutrality. Upon subsequent reversal of the potential to -0.60 V vs. Ag/AgCl, the polymer film was converted to its reduced, neutral form and the arsenate ions were expelled into a smaller volume (200 μL) Of de-ionized water for analysis using flow injection with inductively coupled plasma mass spectrometric (ICP-MS) detection.

(74) Theory of analyte extraction by selected porous polymer SPME fibres, Gorecki_T, Yu_XM, Pawliszyn_J, UNIV WATERLOO,DEPT CHEM,WATERLOO,ON N2L 3G1,CANADA UNIV WATERLOO,WATERLOO
CTR GROUNDWATER RES, WATERLOO, ON N2L 3G1, CANADA JN: ANALYST, 1999, Vol. 124, No. 5, pp. 643-649. Extraction of analytes by the new porous polymer solid phase microextraction (SPME) fibres is based on adsorption rather than absorption. The equilibrium theory developed for the liquid poly(dimethylsiloxane) (PDMS) coating does not apply to these coatings. The paper presents theoretical description of the extraction process for adsorption-type fibres, including PDMS-DVB (divinyl benzene), Carbowax-DVB and Carbowax-TR (template resin). The model is based on Langmuir adsorption isotherm. Expressions describing the amount of analyte extracted by the fibre in two- and three-phase systems are presented and discussed. The effect of selected experimental variables is discussed. In general, there is a non-linear dependence between the amount of an analyte extracted by the fibre and its concentration in a sample. The dependence can be approximated by a straight line for low concentrations only. Matrix composition can significantly affect the amount extracted. Interferences co-extracted with the analyte of interest may reduce the amount extracted and the quasi-linear range of the response. Great care should be exercised therefore when performing quantitative analysis with porous polymer SPME fibres. The phenomena discussed are illustrated on an example of benzene and 4-methyl-2-pentanone extraction from water by PDMS-DVB and Carbowax-DVB fibres.

(75) In-tube solid phase micro-extraction-gas chromatography of volatile compounds in aqueous solution, Tan_BCD, Marriott_PJ, Lee_HK, Morrison_PD, ROYAL MELBOURNE INST TECHNOL, DEPT APPL CHEM, GPO BOX 2476V, MELBOURNE, VIC 3001, AUSTRALIA ROYAL MELBOURNE INST TECHNOL, DEPT APPL CHEM, MELBOURNE, VIC 3001, AUSTRALIA NATL UNIV SINGAPORE, DEPT CHEM, SINGAPORE 119260, SINGAPORE JN: ANALYST, 1999, Vol. 124, No. 5, pp. 651-655. This paper describes the use of conventional coated capillary gas chromatography columns for sorption of organic solutes from aqueous solution, with subsequent gas chromatographic analysis. The essential principles are similar to those of solid phase extraction (SPE) and solid phase micro-extraction (SPME); this approach may be referred to as in-tube solid phase micro-extraction (ITSPME). The technique was evaluated using toluene in water as the initial test solute, and a mixture of BTEX solutes (benzene, toluene, ethylbenzene, xylenes) in Milli-Q water was used to further characterise ITSPME. A 1 m length of capillary GC column was used for sorption of analytes from aqueous solution passed through the capillary by using nitrogen pressure. Collection of small fractions of aqueous solution issuing from the capillary enabled a sorption profile to be generated, with initial fractions depleted in analyte. A Boltzmann curve could be fitted to the sorption profile data, exhibiting good agreement with experimental data. For recovery of sorbed toluene, a single 100 µL aliquot of hexane was passed through the column as a stripping solvent. The back-extraction step was quantitative. Equilibrium extraction of solutes shows that the total amount of recovered solute is proportional to its initial concentration in the extracted aqueous solution and allows distribution constants to be readily estimated. For BTEX solutes, K values were similar to those reported for SPME and literature K-ow values. For toluene, log K decreases from 2.47 to 1.48 when the sorption column temperature increases from 20 to 30 degrees C; adding salt or reducing the pH of the aqueous solution increases the degree of extraction of phenols, agreeing with general considerations on solute partitioning behaviour.

(76) Studies of the composition of distillates from leachate by gas chromatography mass spectrometry coupled to solid-phase microextraction, Saba_A, Pucci_S,
Every day municipal solid waste landfills produce huge amounts of a liquid waste, called leachate, generated mainly by water washing away of the solid waste. Leachate is substantially water containing several organic and inorganic pollutants, usually at trace levels, and must be collected and treated for the maintenance or the landfill. We have studied, on a laboratory scale, an evaporation process for concentration of the leachate, capable of providing a distillate suitable for disposal into surface waters. The distillate was checked for the usual pollution parameters, of which chemical oxygen demand (COD) was the main one. Analysis by gas chromatography/mass spectrometry (GC/MS) was used to identify the organic pollutants, and so to define if toxic substances were present. Solid phase microextraction (SPME) was used to extract the organics from water, by both headspace and immersion methods. We examined the distillates obtained from untreated leachate and also after acidification to pH 4 and basification to pH 10. It was possible to identify several compounds such as phthalates, linear and cyclic unsaturated alcohols, alkylphenols, carbonyl polycyclic compounds, etc. Such compounds were also present in the starting leachate. When the evaporation process was applied to acidified leachate, the composition of the distillate was very similar except for the presence of some aliphatic carboxylic acids not present in the other headspace products, and which could account for the higher COD values of the distillates from acidified leachate.
examine an intermediate waste treatment process that involves adding an electrolyte
(NaCl) at increased temperatures to a single-phase microemulsion (SPME) waste. An in
situ flushing test performed at a Superfund site at Hill AFB, UT, was the source of the
SPME waste. The produced fluids from extraction wells included constituents of a
complex nonaqueous phase liquid (NAPL) extracted from the shallow aquifer, as well
as the surfactant- cosurfactant mixture (3.0% Brij 97, 2.5% n-pentanol) injected to
enhance NAPL solubility. The treatment method is based on separation of the SPME
waste into two immiscible phases: a hydrophobic coil-rich phase, and a hydrophilic
water-rich phase. Laboratory data indicated that at higher temperatures, lower amounts
of salt were required to produce similar levels of volumetric phase separation of the
SPME waste. The volumetric separations (aqueous/total) were on the order of similar to
0.95 +/- 0.01 for samples taken during the first pore volume, and a composite volume of
the flushing experiment. Partitioning of several NAPL constituents into the organic
phase was usually greater than 96% of the mass present in the effluent SPME waste. A
cost analysis suggests potential economic advantages of this intermediate waste
management process.

(79) An improved interface for coupling solid-phase microextraction (SPME) to high
performance liquid chromatography (HPLC) applied to the analysis of explosives,
Wu_LM, Almirall_JR, Furton_KG, FLORIDA INT UNIV,DEPT
CHEM,MIAMI,FL,33199 FLORIDA INT UNIV,INT FORENS RES
INST,MIAMI,FL,33199, HRC-JOURNAL OF HIGH RESOLUTION

Article solutions AU: Yang_JS, Her_JW NA: CHUNG YUAN CHRISTIAN
UNIV,DEPT CHEM,CHUNGLI 32023,TAIWAN, ANALYTICAL CHEMISTRY,
1999, Vol.71, No.9, pp.1773-1779 . The application of the principle of solid-phase
microextraction (SPME) to attenuated total reflectance (ATR) infrared (TR) probes can
provide a convenient and sensitive way to detect volatile organic compounds (VOCs) in
aqueous solutions. In this paper a new method to increase the performance of this type
of sensing device is proposed. A stream of gas purges out VOCs from aqueous solution.
These compounds are directed to an internal-reflection sensor. Several advantages are
recognized by this new method as compared with a conventional liquid probe; these
include a longer lifetime for the probe, higher selectivity in the detection of VOCs, less
limitation in the sample volume, and easier regeneration of the sensing probe.

(80) Microwave mediated distillation with solid-phase microextraction: determination
of off-flavors, geosmin and methylisoborneol, in catfish tissue, Zhu_M, Aviles_FJ,
Conte_ED, Miller_DW, Perschbacher_PW, WESTERN KENTUCKY UNIV,DEPT
CHEM,BOWLING GREEN,KY,42101 NATL CTR TOXICOL RES,DIV
CHEM,JEFFERSON,AR,72079 UNIV ARKANSAS,AQUACULTURE EXPT
STN,PINE BLUFF,AR,71601 JN: JOURNAL OF CHROMATOGRAPHY A, 1999,
Vol.833, No.2, pp.223-230. Presented is a rapid distillation device for use with solid-
phase microextraction (SPME). We apply this device specifically for determining two
semivolatile off-flavor compounds, methylisoborneol and geosmin, in channel catfish.
The presence of these two compounds in channel catfish filets results in unwelcome
tastes. In the presented procedure, a catfish tissue sample is placed within a sample
container located inside the microwave device. Microwave radiation is applied and
distillates formed migrate through a condenser via a purge gas and are collected in a
sample vial. A SPME fiber is placed within the stirred collected distillate and
methyliborneol and geosmin are extracted. Qualitative and quantitative results of these extractions are obtained using a gas chromatograph-ion trap mass spectrometer. This solventless technique results in detection limits far below the human threshold for these off-flavor compounds in channel catfish.

(81) Determination of homocysteine and its related compounds by solid-phase microextraction-gas chromatography-mass spectrometry, Myung_SW, Kim_M, Min_HK, Yoo_FA, Kim_KR, KOREA INST SCI & TECHNOL BIOANAL & BIOTRANSFORMAT RES CTR, POB 131, SEOUL 130650, SOUTH KOREA SUNGSHIN WOMENS UNIV, DEPT CHEM, SEOUL 136742, SOUTH KOREA SUNG KYUN KWAN UNIV, COLL PHARM, SUWON 440746, SOUTH KOREA, JOURNAL OF CHROMATOGRAPHY B, 1999, Vol. 727, No. 1-2, pp. 1-8. The purpose of this study was to develop a simple and accurate analytical method to determine homocysteine (Hcy), cysteine (Cys), and methionine (Met) in aqueous samples. Until now, the most frequently used method for the assay of Hcy, Cys, and Met has been high-performance liquid chromatography with fluorescence detection after fluorescent tagging. The newly developed method involves the employment of the SPME (solid-phase microextraction) technique together with GC-MS. For application to a gas chromatographic system, alkyl formate derivatives were prepared in the form of N(O,S)-alkoxycarbonyl alkyl ester with the analytes in the aqueous samples. The optimum derivatizing reagent for N(O,S)-alkoxycarbonyl alkyl ester was chosen by comparing the efficiency of the derivatized analytes in a GC through the SPME method and liquid-liquid extraction. The optimum conditions of the SPME system for the analytes derivatized with N(O,S)-ethoxycarbonyl propyl ester in the aqueous matrix were pH 3.0 and no salt, and 30 min equilibration time using an 85 μm PA (polyacrylate) fiber. The developed method is inexpensive, easy and rapid.

(82) New coating surfaces of fibers for solid-phase microextraction, Ligor_M, Scibiorek_M, Buszewski_B, NICHOLAS COPERNICUS UNIV, FAC CHEM, DEPT ENVIRONM CHEM, GAGARIN STR 7, PL-87100 TORUN, POLAND, NICHOLAS COPERNICUS UNIV, FAC CHEM, DEPT ENVIRONM CHEM, PL-87100 TORUN, POLAND, POLISH ACAD SCI, MOL & MACROMOL CTR RES, PL-90363 LODZ, POLAND, JOURNAL OF MICROCOLUMN SEPARATIONS, 1999, Vol. 11, No. 5, pp. 377-383. In this paper, some theoretical and practical aspects of solid-phase microextraction coated fibers will be discussed in detail. The surfaces of a series of prepared fibers have been characterized by chromatographic methods. The following fibers were tested: ethoxy-polydimethylsiloxane coated fibers (PDES), polyurethaneacrylate coated fiber, fused silica fiber, and fused silica fiber after etching with hydrofluoric acid. Sorption properties for each fiber were examined using BTEX standards in methanol. The time needed for the analyte to reach equilibrium between the sample and the fiber was determined. The extraction time profiles for individual fiber coatings were established by plotting the extracted mass versus the extraction time. The efficiencies of extraction for the tested fibers and for polydimethylsiloxane (PDMS) used as a reference fiber were compared. The distribution constants of the polymer coating/aqueous phase.

(83) Solid-phase microextraction of the antifouling Irgarol 1051 and the fungicides dichlofluanid and 4-chloro-3-methylphenol in water samples, Penalver_A, Pocurull_E, Borrell_F, Marce_RM, UNIV ROVIRA & VIRGILI, DEPT QUIM ANALIT & QUIM ORGAN, IMPERIAL TERRACO 1, TARRAGONA 43005, SPAIN, UNIV ROVIRA &
Three pesticides usually added to paint formulations, Irgarol 1051, dichlofluanid and 4-chloro-3-methylphenol, were determined by solid-phase microextraction (SPME) with 85-μm polyacrylate fibers and gas chromatography-mass spectrometry. The parameters affecting the SPME process (the pH, the addition of salt to the sample, and the time and temperature of the absorption step) were optimized. The method developed was applied to the analysis of water samples from Ebro river, marinas and fishing peas. The method enables these compounds to be detected at concentrations between 0.2 and 3.0 μg l⁻¹ under full scan conditions and between 0.05 and 8.08 μg l⁻¹ under SIM mode.

Degradation of palmitic (hexadecanoic) acid deposited on TiO₂-coated self-cleaning glass: kinetics of disappearance, intermediate products and degradation pathways, Romeas_V, Pichat_P, Guillard_C, Chopin_T, Lehaut_C, ECOLE CENT LYON,CNRS,URA,BP 163,F-69131 ECULLY,FRANCE ECOLE CENT LYON,CNRS,URA,F-69131 ECULLY,FRANCE RHONE POULENC,CTR RECH,F-93308 AUBERVILLIERS,FRANCE, NEW JOURNAL OF CHEMISTRY, 1999, Vol.23, No.4, pp.365-373. Self-cleaning glass was prepared by depositing anatase nanoparticles as a transparent film onto glass previously coated by a barrier layer. A photoreactor was built to evaluate the efficiency. Palmitic acid, chosen as a compound representing stains from various sources and sprayed over these plates to form an uniform layer of ca. 580 nm thickness, was shown to disappear at a rate of ca. 60 nm h⁻¹ under UV irradiation corresponding to the average solar radiant power at midlatitude. That clearly demonstrated that this glass is efficient enough, at least with this type of grease stain, to implement its use. Our main efforts explored the identification of palmitic acid degradation products under these conditions by use of chromatographic methods, various solvents for recovering products on the glass, and various adsorbents (cartridges or SPME) for gas-phase analysis. The 39 products identified revealed the gradual splitting of the palmitic acid chain yielding the whole series of linear aldehydes and carboxylic acids, some alkanes and two alcohols. In the closed photoreactor, complete mineralization was achieved. When the photoreactor atmosphere was renewed every hour, formaldehyde, acetaldehyde and acetone reached the highest concentrations in the gas phase. Mechanisms involving the initial attack of palmitic acid either by photogenerated holes or by hydroxyl radicals with subsequent formation of alkylperoxy radicals, hydroperoxides and tetroxides are discussed to account for the products. PA: 10839 FR;VITRAGE_G{1997} 737513 EP;FUJISHIMA_A{APPL 1996}.

Determination of organophosphorus pesticides in soil by headspace solid phase microextraction, Ng_WF, Teo_MJK, Lakso_HA, DSO NATL LABS, 20 SCI PK DR,SINGAPORE 118230,SINGAPORE FOA,DIV NBC DEF,S-90182 UMEA,SWEDEN JN: FRESENIUS JOURNAL OF ANALYTICAL CHEMISTRY, 1999, Vol.363, No.7, pp.673-679. Headspace solid-phase microextraction (SPME) has been developed for the analysis of common organophosphorus pesticides in soil. Factors such as adsorption-time, sampling temperature and matrix modification by addition of water were carefully considered to optimize the extraction efficiency. This technique could achieve limits of detection of 143 ng/g for Malathion and Parathion, and 28.6 ng/g for Phorate, Diazinon and Disulfoton in humic soil when the extracted sample was analyzed by gas chromatography-flame ionization detector (GC-FID). Lower limits of detection of 28.6 ng/g for Malathion and Parathion, and 14.3 ng/g for Phorate, Diazinon and Disulfoton can be achieved by analyzing the extracted sample
with gas chromatography / mass spectrometric detector (GC/MS). As the extraction efficiency was generally better when analyzing sandy soil, the limits of detection are envisaged to be even better for such a matrix. The technique was found to be reliable with good precision of about 6.5% RSD for the sandy soil and about 15% for the humic material. The poorer precision of extraction from the humic material is probably related to the poorer homogeneity of this material. The linearity of extraction was good with linear calibration in the range of 0.143 to 28.6 µg/g. Finally, headspace SPME was compared to aqueous extraction of soil followed by SPME (LE-SPME). The recoveries obtained by headspace SPME were comparable to those from liquid-liquid extraction of soil followed by SPME. However, the analysis of headspace SPME has less background interference. Perhaps, the greatest advantage of this technique is its non-destructive nature so that it is possible to perform further laboratory analysis of the samples after headspace SPME has been carried out.

(86) Determination of polar pesticides in soil by solid phase microextraction coupled to high-performance liquid chromatography-electrospray mass spectrometry, Moder_A, Popp_P, Eisert_R, Pawlisyn_J, CTR ENVIRONM RES LEIPZIG HALLE LTD, DEPT ANALYT CHEM, PERMOUSERSTR 15, D-04318 LEIPZIG, GERMANY UNIV WATERLOO, DEPT CHEM, WATERLOO, ON N2L 3G1, CANADA, FRESENIUS JOURNAL OF ANALYTICAL CHEMISTRY, 1999, Vol.363, No.7, pp.680-685. The determination of carbamate and triazine pesticides from soil leachates and slurries was investigated using solid phase microextraction (SPME) coupled to high-performance liquid chromatography-electrospray / mass spectrometry (HPLC-ESI/MS). SPME was carried out using fibres with a newly developed 50 µm Carbowax/template coating which are suitable for relatively polar analytes. These fibers exhibit precisions better than 10% RSD, and are resistant against high contents of organic solvents during desorption. The technique shows a high sampling frequency resulting in an increasing sample throughput.

(87) Application of solid-phase microextraction to monitoring indoor air quality, Gorlo_D, Zygmunt_B, Dudek_M, Jaszek_A, Pilarczyk_M, Namiesnik_J, GDANSK TECH UNIV, FAC CHEM, 11-12 G NARutowICZA ST, PL-80952 GDANSK, POLAND GDANSK TECH UNIV, FAC CHEM, PL-80952 GDANSK, POLAND IN: FRESENIUS JOURNAL OF ANALYTICAL CHEMISTRY, 1999, Vol.363, No.7, pp.696-699. Practical application of Solid-Phase Microextraction (SPR IE) for the assessment of the quality of indoor air is presented. SPME was used to sample selected organic pollutants (carbon tetrachloride, benzene, toluene, chlorobenzene, p-xylene and n-decane). An SPME fiber was coated with a 100 µm film of polydimethylsiloxane. The analytes extracted were analysed with a gas chromatograph directly coupled with a mass spectrometer (GCMS). The method was used to assess the indoor air quality in a few selected flats. The concentrations ranged from below detection limits to 6.9 mg/m(3) for benzene depending on the flat; they were relatively high for newly built or freshly renovated flats.

(88) Headspace solid-phase microextraction for the determination of trace levels of taste and odor compounds in water samples, Bao_ML, Griffini_O, Burrini_D, Santianni_D, Barbieri_K, Mascini_M, UNIV FLORENCE, DEPT PUBL HLTH EPIDEMIOLOGICA & ENVIRONM ANALYT CHEM, VIA G CAPponi 9, I-50121 FLORENCE, ITALY UNIV FLORENCE, DEPT PUBL HLTH EPIDEMIOLOGICA & ENVIRONM ANALYT CHEM, I-50121 FLORENCE, ITALY WATER SUPPLY
The use of the headspace solid-phase microextraction (SPME) technique, combined with gas chromatography-ion-trap detection mass spectrometry (GC-ITDMS), for the determination of 34 taste- and odor-causing organic compounds in water is presented. The compounds studied include aliphatic hydrocarbons, aldehydes, ketones and alcohols. The factors affecting the headspace SPME process, such as fiber type, salt addition, stirring, headspace volume and sampling time, were examined. The polydimethylsiloxane-divinylbenzene-coated fiber was found to be effective for the extraction of the compounds studied. The precision of the method was evaluated with spiked bidistilled water and river water samples. The RSDs obtained were similar for both water samples and in the range 4.3-17.1%. Using the standard addition calibration method, the problem of matrix effects observed for river water samples can be reduced. The method showed good linearity over two orders of magnitude of concentration in river water. With 40 ml of water sample, the detection limits were lower than 1 ng l (−1) for 2-methylisoborneol and geosmin, and 0.8-50 ng l(−1) for the other compounds.

A new concept for the measurement of total volatile compound of food, Azodanlou_R, Darbellay_C, Luisier_JL, Villettaz_JC, Amado_R, SWISS FED INST TECHNOL,INST FOOD SCI,ZURICH,SWITZERLAND ECOLE INGN VALAIS,DEPT FOOD TECHNOl & BIOTECHNOL,SION,SWITZERLAND SWISS FED RES STN PLANT PROD,MONTHHEY,SWITZERLAND, ZEITSCHRIFT FUR LEBENSMITTEL-UNTERSUCHUNG UND-FORSCHUNG A-FOOD RESEARCH AND TECHNOLOGY, 1999, Vol.208, No.4, pp.254-258. The aim of our work was to develop a rapid and reliable method for the evaluation of the total volatile fraction of fruits (strawberries, raspberries, tomatoes and apples). Our method consists of trapping the Volatile compounds of fruits on a solid-phase microextraction (SPME) fibre and determining the total amount of the adsorbed substances after desorption in a GC system, without performing any separation. The patterns obtained by using several types of SPME fibre permitted us to differentiate between the total volatile compounds present in the sample depending upon their chemical nature. Using strawberries as a model, we could show that our method: (1) leads to easily reproducible results; (2) allows differentiation between six varieties in a way which is consistent with an hedonic evaluation of these varieties; (3) shows the variation in total volatile compounds between individual fruits. The technique is rapid, practical, cheap, and promising for an objective evaluation of the volatile fraction of fruits.

Solid phase microextraction application in gas chromatography olfactometry dilution analysis AU: Deibler_KD, Acree_TE, Lavin_EH NA: CORNELL UNIV,NEW YORK STATE AGR EXPT STN,DEPT FOOD SCI & TECHNOL,GENEVA,NY,14456 JN: JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY, 1999, Vol.47, No.4, pp.1616-1618 IS: 0021-8561 DT: Article AB: Gas chromatography/olfactometry (GC/O) based on dilution analysis (e.g., CharmAnalysis or aroma extraction dilution analysis) gives an indication of what compounds are most important (most potent) to the aroma of foods. The application of solid phase microextraction to the preparation of samples for GC/O dilution analysis was shown to be feasible by varying the fiber thickness and length to achieve various absorbant volumes.

Artefact-free determination of trihalomethanes in chlorinated swimming-pool water using headspace solid-phase microextraction and gas chromatography LA:
Headspace solid-phase microextraction (headspace SPME) is a rather new technique for the solvent-free extraction and concentration of volatile substances from water into an organic polymer layer covering a fused-silica fiber. In combination with gas chromatography, the method represents a powerful tool for sensitive headspace investigations. As the adsorption of low boiling substances is favoured at low temperatures, the method can be operated at ambient temperature without formation of artefacts. Therefore, the method is ideally suited for the analysis of volatile disinfection by-products in water including several thermolabile THM-precursors. For the artefact-free determination of trihalomethanes it is superior to headspace gas chromatography under the conditions of the German standard method DIN 38407-F5. Compared to chromatography after pentane extraction (DIN 38407-F4), headspace SPME is simpler, less laborious, better reproducible, and, especially for polar, easily water-soluble components, much more sensitive. In addition, it operates solvent-free and can be automated. Using a 100-μm polydimethylsiloxane-coated fiber, the method is linear over at least 2 orders of magnitude and has a relative standard deviation of 2... 7% in the upper ng/L range. With a 65-μm polydimethylsiloxane/divinylbenzene-coating on the fiber, the sensitivity of the method can be extended to limits of quantitation in the low ng/L range. However, this fiber, shows an increased susceptibility to matrix effects as observed in the presence of diisopentyl ether, which can only be compensated by using the method of standard addition. WA: headspace solid-phase microextraction, headspace SPME, disinfection by-products, trihalomethanes artefacts, swimming-pool water.

(92) Determination of chloroethers in aqueous samples using solid-phase microextraction

A method for the determination of di- and tetrachlorinated ethers (haloethers) in aqueous samples using solid-phase microextraction (SPME) combined with capillary GC has been developed. Using 100-μm polydimethylsiloxane fibers, the influence of several parameters on the SPME procedure like the exposure time of the fiber in the aqueous sample, the desorption temperature, and the salt content of the sample have been studied. Salt addition has a strong effect on the extraction efficiency of the haloethers investigated. Working with saturated salt solutions, the factor increase of the peak areas was in the range from 5 to 12. These improvements are accompanied by decreased precision and increased equilibration times. The SPME method combined with several detectors (FID, ECD, MS in SIM mode) was evaluated with respect to detection limits, lineairities, and precisions. Working with salt addition and FID, detection limits of all compounds investigated were in the range of 0.3 to 1.2 ng/L. Using ECD, the LOD values (limits of detection) were only improved for the tetrachlorinated bis(propyl) ethers (< 10 ng/L). Employing mass-spectrometric detection in SIM mode for all chlorinated ethers, detection limits lower than 100 ng/L could be reached. Working with saturated salt solutions, the coefficients of variance solid-phase microextraction, Koch_J, Volker_P, HAMBURG WASSERWERKE GMBH, ZENTRALLAB, BILLHORNER DEICH 2, D-20539 HAMBURG, GERMANY, ACTA HYDROCHIMICA ET HYDROBIOLOGICA, 1997, Vol. 25, No. 4, pp. 179-190 IS: 0323-4320 DT: Article AB: Headspace-analytical
techniques are usually applied to the determination of easily volatile substances in water, whereas semivolatile are generally isolated by liquid-liquid or solid-phase extraction. In the present paper, a method is presented for isolating high boiling polychlorinated biphenyls (PCB) using headspace solid-phase microextraction at elevated temperature. In spite of their low vapor pressure, the analytes are adsorbed very efficiently on a polydimethylsiloxane-coated fiber. Thus, in combination with GC/ECD, a very simple and sensitive solventless determination of PCB is accomplished. Using the simplest possible standard conditions, limits of determination in the lowest nanogram-per-liter range are achieved. Further increased sensitivity down to the ppq (parts per quadrillion) range is possible by stirring and increasing the sample volume and adsorption time. Moderate matrix effects have been observed in some surface and groundwaters.

(94) Determination of organometallic compounds in surface water and sediment samples with SPME-CGC-ICPMS, DSmael_T, Moens_L, Sandra_P, Dams_R, STATE UNIV GHENT, INST NUCL SCI, ANALYT CHEM LAB, PROEFTUINSTR 86,B-9000 GHENT, BELGIUM STATE UNIV GHENT, INST NUCL SCI, ANALYT CHEM LAB, B-9000 GHENT, BELGIUM STATE UNIV GHENT, ORGAN CHEM LAB, B-9000 GHENT, BELGIUM, MIKROCHIMICA ACTA, 1999, Vol.130, No.4, pp.241-251. Organometal compounds of tin, mercury and lead were simultaneously determined in environmental, water and sediment samples by GC-ICPMS. Instead of classical liquid/liquid extractions, solid phase microextraction was used as sampling technique. In this method, the organometallic compounds are in situ derivatised in the aqueous phase and simultaneously extracted onto a polydimethylsiloxane fiber, so that organic solvents are no longer necessary. The sorbed organometals are subsequently released from the fiber in the GC injection liner by thermal desorption. By sampling from the headspace, only the species of interest are sampled and no interfering matrix components are coextracted. With this new method, derivatisation, extraction, preconcentration and injection into the GC takes only 10 min with a minimum of handling steps. Owing to the very low detection limits (0.13-3.7 ng/l as metal) only small sample amounts (25 ml of water, 0.5 g of sediment) are needed for one analysis. Finally, SPME is an inexpensive sampling technique that can be used with standard split/splitless injection systems.

(95) Time-weighted average sampling with solid-phase microextraction device: Implications for enhanced personal exposure monitoring to airborne pollutants AU: Martos_PA, Pawliszyn_J NA: UNIV WATERLOO, DEPT CHEM, WATERLOO, ON N2L 3G1, CANADA JN: ANALYTICAL CHEMISTRY, 1999, Vol.71, No.8, pp.1513-1520 IS: 0003-2700 DT: Article AB: The solid-phase microextraction (SPME) device is used as a time-weighted average (TWA) sampler for gas-phase analytes by retracting the coated fiber a known distance into its needle housing during the sampling period. Unlike in conventional spot sampling with SPME, the TWA sampling approach does not allow the analytes to reach equilibrium with the fiber coating, but rather they diffuse through the opening in the needle to the location of the sorbent. The amount of analytes accumulated over time gives the measurement of the average concentration to which the device was exposed to. Depending on the sorbent used as the sink, TWA sampling for various analytes is possible with times ranging from 15 min to at least 16 h. Both the poly(dimethylsiloxane) (PDMS) and poly(dimethylsiloxane)/divinylbenzene (PDMS/DVB) fiber coating phases were tested, with the latter employing on-fiber
derivatization for reactive carbonyl compounds, e.g., formaldehyde. Described herein are the theoretical and practical considerations for using the SPME device as a TWA sampler.

(96) Determination of organophosphorus pesticides in water using SPME-GC-MS. Silva_FC, Cardeal_ZD, deCarvalho_CR, UNIV FED MINAS GERAIS,DEPT QUIM, BR-31270901 BELO HORIZONT, MG, BRAZIL FUNDACAO CTR TECNOL MINAS GERAIS, LAB ANALISE AMBIENTAL, BR-31170000 BELO HORIZONT, MG, BRAZIL UNIV FED MARANHAO, CT, DEPT QUIM, BR-65080040 SAO LUIS, MA, BRAZIL, QUIMICA NOVA, 1999, Vol.22, No.2, pp.197-200 IS: 0100-4042 DT: Article AB: Solid-phase microextraction (SPME) has been applied to direct extraction of 11 organophosphorus pesticides in water using a 100 μm fiber polydimethylsiloxane. The method was evaluated with respect to time of exposure, detection limits (LODs), linearity and precision. The detection limits (S/N = 3) depend on each pesticide and vary about ng/L levels. The linearity was satisfactory with coefficients of correlation usually greater than 0.993. The precision of the method was determined by extraction from 4.0 μg/L aqueous standard with coefficients of variation between 5.7 to 17.2%.

(96) Solid-phase microextraction, Prosen_H, ZupanicKralj_L, UNIV LJUBLJANA, FAC CHEM & CHEM TECHNOL, ASKERCEVA 7, SLO-1000 LJUBLJANA, SLOVENIA, TRAC-TRENDS IN ANALYTICAL CHEMISTRY, 1999, Vol.18, No.4, pp.272-282. In recent years, much attention in analytical chemistry has been paid to sample preparation techniques, especially those which minimise the consumption of organic solvents. One of the most promising of these, solid-phase microextraction (SPME), is presented in both its theoretical and practical aspects. Conditions which affect its performance are assessed, as are the problems which may arise from its use. Finally, some typical applications are listed, highlighting the method's sensitivity and precision, and the range of samples where SPME can be used successfully.

(97) Pulsed electric field processing effects on flavor compounds and microorganisms of orange juice, Jia_MY, Zhang_QH, Min_DB, OHIO STATE UNIV, DEPT FOOD SCI & TECHNOL, 2121 FYFFE RD, COLUMBUS, OH, 43210 OHIO STATE UNIV, DEPT FOOD SCI & TECHNOL, COLUMBUS, OH, 43210, FOOD CHEMISTRY, 1999, Vol.65, No.4, pp.445-451. The headspace flavor compounds of fresh squeezed orange juice processed by pulsed electric field (PEF) at 30 kV/cm for 240 or 480 μs, or heat at 90 degrees C for 1 min were isolated by a solid phase microextraction (SPME) coating and separated by gas chromatography. The average losses of flavor compounds in orange juice processed by 240, 480 ps PEF and heat process were 3.0%, 9.0% and 22.0%, respectively (P < 0.05). The flavor loss was mainly due to vacuum degassing in the PEF process. The total plate counts of control, 240, 480 μs PEF, and heat processed orange juice were 5400, 21, 19, and 4, respectively. The yeast and mold counts of control, PEF for 240, 480 μs and heat processed orange juice were 2800, 15, 9, and 4, respectively.

(98) Extraction of methylxanthines from human body fluids by solid-phase microextraction, Kumazawa_T, Seno_H, Lee_XP, Ishii_A, WatanabeSuzuki_K, Sato_K, Suzuki_O, SHOWA UNIV, SCH MED, DEPT LEGAL MED, SHINAGAWA KU, 1-5-8 HATANODAI, TOKYO 1428555, JAPAN HAMAMATSU UNIV, SCH
Four methylxanthines, caffeine, theobromine, paraxanthine and theophylline, have been found extractable from human whole blood and urine samples by solid-phase microextraction (SPME) with a Carbowax/divinylbenzene-coated fiber. Their determination was made by using capillary gas chromatography with nitrogen phosphorus detection. Extraction efficiency of the methylxanthines was 0.01-0.047% for whole blood, and 0.05-0.229% for urine, respectively. The regression equations for the compounds showed excellent linearity in the range 1.88-60 μg ml(-1) for whole blood and urine samples, except for caffeine (0.31-20 μg ml(-1) for whole blood and 0.16-20 μg ml(-1) for urine). The detection Limits for each of the compounds were 0.2-0.9 and 0.06-0.7 μg ml(-1) for whole blood and urine, respectively. The coefficients of within-day variation in terms of extraction efficiency for all compounds in whole blood and urine samples were 3.2-9.3% and 2.6-8.4%, respectively. The data obtained for the actual determination of four methylxanthines in a male subject after ingestion of coffee or cocoa were also presented.

Volatiles of bracket fungi Fomitopsis pinicola and Fomes fomentarius and their functions as insect attractants, Faldt_J, Jonsell_M, Nordlander_G, BorgKarlson_AK, ROYAL INST TECHNOL,DEPT CHEM,S-10044 STOCKHOLM,SWEDEN SWEDISH UNIV AGR SCI,DEPT ENTOMOLS,S-7507 UPPSALA,SWEDEN, JOURNAL OF CHEMICAL ECOLOGY, 1999, Vol.25, No.3, pp.567-590. Volatiles released from fruiting bodies of the polypores Fomitopsis pinicola and Fomes fomentarius (Polyporaceae) were collected by entrainment and SPME techniques and analyzed by GC-MS. The most significant difference between the two species was found in the terpene fraction. F. fomentarius emitted a more complex blend, with more than 10 sesquiterpenes. During the sporulating phase, the release of (R)- and (S)-oct-1-en-3-ol, octan-3-one, and some sesquiterpene hydrocarbons (mainly beta-barbatene) increased in F: pinicola, whereas in F. fomentarius the release of octan-3-one, cis-furanoid linalool oxide, beta-phellandrene, beta-myrcene, and several sesquiterpene hydrocarbons increased. beta-Barbatene was identified for the first time in fungi. Chopping of the fruiting bodies altered the odor composition more in F: pinicola. Five volatiles giving a typical fungal odor (rac-oct-1-en-3-ol, nonan-1-ol, rac-octan-3-ol, octan-1-ol, and octan-3-one) were tested for insect attraction in the field. Females of the three wood-living generalist beetles Malthodes fuscus, Anaspis marginicollis, and A. rufilabris and both sexes of the moth Epinotia tedella were attracted to rac-oct-1-en-3-ol. The generalist predator on fungus-insects Lordithon lunulatus was attracted to rac-oct-1-en-3-ol and octan-3-one in combination. Previous results regarding the host-specific attraction of beetles to the odors emanating from chopped fruiting bodies of R pinicola and F. fomentarius are discussed in the light of this investigation.

Determination of hydroxyaromatic compounds in water by solid-phase microextraction coupled to high-performance liquid chromatography, Wu_YC, Huang_SD, NATL TSING HUA UNIV,DEPT CHEM,Hsinchu 30043,TAIWAN, JOURNAL OF CHROMATOGRAPHY A, 1999, Vol.835, No.1-2, pp.127-135. Solid-phase microextraction (SPME) coupled with high-performance liquid chromatography (HPLC) for the analysis of hydroxyaromatic compounds is described. Three kinds of fibers [50 μm carbowax-templated resin (CW-TPR), 60 μm polydimethylsiloxane-divinylbenzene (PDMS-DVB) and 85 μm polyacrylate (PA) fibers] were evaluated.
CW-TPR and PDMS-DVB were selected for further study. The parameters of the desorption procedure (such as desorption mode, the composition of the solvent for desorption and the duration of fiber soaking) were studied and optimized. The effect of the structure and physical properties of analytes, carryover, duration of absorption, temperature of absorption, pH and ionic strength of samples were also investigated. The method was applied to environmental samples (lake water) using a simple calibration curve.

(101) Simultaneous determination of Hg(II) and alkylated Hg, Pb, and Sn species in human body fluids using SPME-GC/MS-MS, Dunemann_L, Hajimiragha_H, Begerow_J, MED INST UMWELTHYG,DEPT ANALYT CHEM, HENNEKAMP 50, D-40225 DUSSELDORF, GERMANY, FRESENIUS JOURNAL OF ANALYTICAL CHEMISTRY, 1999, Vol.363, No.5-6, pp.466-468. A GC/MS-MS method for the determination of Hg(II) and alkylated Hg, Pb, and Sn species in human urine is described. Separation and identification of the metal species are performed by capillary gas chromatography coupled with an ion-trap mass spectrometer with electron impact ionization in the tandem-MS mode. For sample preparation a very promising technique was applied that is based on a derivatization with sodium tetraethylborate followed by headspace solid phase microextraction (SPME). Operation of the used ion trap in the tandem-MS mode yields in improved detection limits because of a signal-to-noise ratio that is at least one order of magnitude better than in the MS mode. The detection limits in real matrices like urine are between 7 and 22 ng/L for all species investigated. Urinary levels of inorganic Hg in non-occupationally exposed persons with and without dental amalgam were found to be between 01.4 μg/L. A reference material ("ClinRep, Level I") was used for quality assurance. Compared to the coupling of GC with ICP-MS ("inorganic" MS), the advantage of the proposed method using an "organic" MS is that (i) the species can be directly identified via their precursor and daughter ions and (ii) analysis can be performed with a commercially available hyphenated technique at moderate costs and needs no lab-made interfacing. Moreover, it offers a real multi-element/multi-species capability with low detection limits and a minimum of sample preparation.

(102) Researchers are giving PME a second look AU: Comello_V JN: R&D MAGAZINE, 1999, Vol.41, No.2, pp.44-45

(103) TI: Headspace sampling of whey protein concentrate solutions using solid-phase microextraction, LeQuach_M, Chen_XD, Stevenson_RJ, UNIV AUCKLAND, SCH BIOL SCI, BIOTECHNOL TEACHING PROGRAM, 20 SYMONDS ST, PRIVATE BAG 92019, AUCKLAND 1, NEW ZEALAND UNIV AUCKLAND, SCH BIOL SCI, BIOTECHNOL TEACHING PROGRAM, AUCKLAND 1, NEW ZEALAND UNIV AUCKLAND, SCH ENGN, DEPT CHEM & MAT ENGN, FOOD SCI & PROC ENGN GRP, AUCKLAND 1, NEW ZEALAND UNIV AUCKLAND, DEPT CHEM, AUCKLAND, NEW ZEALAND, FOOD RESEARCH INTERNATIONAL, 1998, Vol.31, No.5, pp.371-379. Whey protein concentrate (WPC) represents a potentially substantial source of nutritious, functional protein ingredient for many traditional and novel food products. Characterisation of WPC's volatile profile plays an important role in the manipulation of its flavour perception for various applications. The combination of solid-phase microextraction (SPME) as a headspace sampling technique and gas chromatography/mass spectrometry for compound separation / identification have proven to be convenient and sensitive. An optimisation exercise of the headspace
SME (HS- SPME) technique with WPC solutions is described: the effects of SPME fibre polarity, sampling time, temperature and equilibration period have been investigated.

(104) Solubility and partitioning studies with polycyclic aromatic hydrocarbons using an optimized SPME procedure, Paschke_A, Popp_P, Schuermann_G, UFZ CENT ENVIRONM RES,DEPT CHEM ECOTOXICOL,PERMOSERSTR 15,D- 04318 LEIPZIG,GERMANY UFZ CENT ENVIRONM RES,DEPT ANALYT CHEM,D-04318 LEIPZIG,GERMANY, FRESENIUS JOURNAL OF ANALYTICAL CHEMISTRY, 1999, Vol.363, No.4, pp.426-428. In order to determine the water solubility (S-w) and octanol/water partition coefficient (K-ow) of polycyclic aromatic hydrocarbons, we have optimized the direct solid-phase microextraction (SPME) of selected compounds (fluoranthene (FLU), phenanthrene (PHE), pyrene (PYR), benz[a]anthracene (BaA), benz[a]pyrene (BaP), and coronene) from the matrices water and octanol-saturated water. By the use of a 100 mu m polydimethylsiloxane fibre and magnetic stirring of the sample with glass-coated mini-impellers in combination with gas chromatography we obtained limits of determination (GC-MS) comparable to standard HPLC procedures. Only coronene could not be quantified. The determined S-w of FLU agree with reference data; for B[a]P we have obtained a 2 to 3 times higher value than described in recent literature. The obtained K-ow values are close to reference data for both single components. For a mixture of FLU, PHE, PYR, and B[a]A the measured K-ow values are 0.2-0.3 log units below tabulated values for the single components.


(106) Partition infrared method for total gasoline range organics in water based on solid phase microextraction, Stahl_DC, Tilotta_DC, UNIV N DAKOTA,DEPT CHEM,POB 9024,GRAND FORKS,ND,58202 UNIV N DAKOTA,DEPT CHEM,GRAND FORKS,ND,58202, ENVIRONMENTAL SCIENCE & TECHNOLOGY, 1999, Vol.33, No.5, pp.814- 819 A new method is described for determining total gasoline-range organics (TGRO) in water that combines solid-phase microextraction (SPME) and infrared (IR) spectroscopy. In this method, the organic compounds are extracted from 250-mL of water into a small square (3.2 cm x 3.2 cm x 130 mu m thick) of Teflon PFA film. This film, a perfluoroalkoxyethylene polymer, lacks C-H bonds and makes it possible to quantitate the extracted organics directly in it via their C-H stretching vibrations. Three gasoline-range fuels, unleaded gasoline, aviation gas, and lighter fuel (petroleum naphtha), were chosen to evaluate the SPME/IR procedure. Preliminary experiments show that method detection limits are in the 0.5-1.5 ppm range for spiked solutions, and precision is relatively good (6-11% RSDs). Linear dynamic ranges of calibration extend to the water solubility limits for all fuels studied. Finally, the potential of this SPME/IR method for determining TGRO in natural "real world" water samples was investigated by extracting wastewater contaminated with gasoline. In this procedure, a commercially available gas chromatography standard was used to calibrate the SPME/IR method. The results obtained from the SPME/IR determination of the TGRO in two wastewater samples...
were in reasonable agreement with those obtained from standard purge- and-trap gas chromatographic analysis.

(107) Cryo-trapping/SPME/GC analysis of cheese aroma, Jaillais_B, Bertrand_V, Auger_J, UNIV TOURS,IRBI,UPRES A CNRS 6035,PARC GRANDMONT,F-37200 TOURS,FRANCE UNIV TOURS,IRBI,UPRES A CNRS 6035,F-37200 TOURS,FRANCE UNIV TOURS,SAVIT,F-37200 TOURS,FRANCE, TALANTA, 1999, Vol.48, No.4, pp.747-753 IS: 0039-9140 DT: Article AB: The advantages of combined cold-trapping of cheese volatiles and solid-phase microextraction-GC are demonstrated. This method is simple, cheap, compatible with classic identification equipment, and allows in-situ sampling.

(108) Solid phase microextraction of pesticide residues from strawberries, Hu_RW Hennion_B, Urruty_L, Montury_M, LPTCSN,EPCA,BP 1043,F-24001 PERIGUEUX,FRANCE LPTCSN,EPCA,F-24001 PERIGUEUX,FRANCE , FOOD ADDITIVES AND CONTAMINANTS, 1999, Vol.16, No.3, pp.111-117 . A new solid phase microextraction method for the determination of pesticide residues in strawberries for 16 commonly used compounds was described. The strawberries were crushed and centrifuged. An aliquot of the well agitated aqueous supernatant (4ml was extracted with a fibre coated with polydimethylsiloxane (PDMS, 100 mum) for 45 min at room temperature. Identification and quantification were achieved using a gas chromatography-mass spectrometry (GC-MS) system and selective ion monitoring (SIM). The method was tested for the following pesticides: carbofuran, diethofencarb, penconazole, hexaconazole, metalaxyl, folpet, bromopropylate, dichlofluanid, alpha-endosulfan, beta-endosulfan, parathion ethyl, procymidone, iprodione, vinclozolin, myclobutanil and chlorothalonil. Limits of detection, repeatability and linearity for standard calibration in strawberries were obtained. Positive and negative effects of the matrix between the extracting solution of strawberries and water were observed. Stabilities of these compounds in the extracting solution of strawberries were determined. The solvent-free SPME procedure was found to be quicker and more cost effective than the solvent extraction methods commonly used.


(110) Validation of a solid-phase microextraction method for the determination of organophosphorus pesticides in fruits and fruit juice, Simplicio_AL, Boas_LV, INST BIOL EXPT & TECNOL,APARTADO 12,P-2780 OEIRAS,PORTUGAL INST SUPER TECN,P-1096 LISBON,PORTUGAL UNIV NOVA LISBOA,INST TECNOL QUIM & BIOL,P-2780 OEIRAS,PORTUGAL, JOURNAL OF CHROMATOGRAPHY A, 1999, Vol.833, No.1, pp.35-42 .A method for the determination of organophosphorus pesticides (diazinon, fenitrothion, fenthion, quinalphos, triazophos, phosalon and pyrazophos) in fruit (pears) and fruit juice samples was developed and validated. The samples were diluted with wafer, extracted by solid-phase microextraction (SPME) and analysed by gas chromatography (GC) using a flame photometric detector in phosphorous mode. Limits of detection of the method for fruit and fruit juice matrices were below 2 mu g/kg for all pesticides. Relative
standard deviations for triplicate analyses of samples fortified at 25 μg/kg of each pesticide were not higher than 8.7%. Recovery tests were performed for concentrations between 25 and 250 μg/kg. Mean recoveries for each pesticide were all above 75.9% and below 102.6% for juice, and between 70 and 99% for fruit except for pyrazophos in the fruit sample (with mean recovery of 53%). Therefore, the proposed method is applicable in the analysis of pesticides in fruit matrices and the use of the method in routine analysis of pesticide residues is discussed.

(111) Analysis of diacetyl in wine using solid-phase microextraction combined with gas chromatography mass spectrometry, Hayasaka_Y, Bartowsky_EJ, AUSTRALIAN WINE RES INST,POB 197,GLEN OSMOND,SA 5064,AUSTRALIA, JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY, 1999, Vol.47, No.2, pp.612-617. Analytical difficulties in the rapid and accurate determination of diacetyl (DA), an important flavor compound in wine, at low concentrations have been overcome by the use of solid-phase microextraction (SPME) with deuterated diacetyl-d(6) (d6-DA) as an internal standard followed by gas chromatography-mass spectrometry (GC-MS). The CC-MS analyses showed that the values of the ion response ratio of DA to d6-DA were consistent regardless of the conditions of SPME headspace and were not influenced by the presence of sulfur dioxide in wine. The quantitation value of DA was represented as the concentration of free plus bound with sulfur dioxide forms of DA. The detection limit of DA in wine was as low as 0.01 μg/mL with linearity through to 10 μg/mL.

(112) SPME-MS-MVA as an electronic nose for the study of off-flavors in milk, Marsili_RT, DEAN FOODS TECH CTR, POB 7005,ROCKFORD,IL,61125, JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY, 1999, Vol.47, No.2, pp.648-654. A new technique using solid-phase microextraction, mass spectrometry, and multivariate analysis (SPME-MS-MVA) was developed for the study of off-flavors in milk. The analytical column of a GC/MS system was replaced with a 1-m deactivated fused-silica column, which served as a transfer line to deliver volatiles extracted from milk samples with a Carboxen-SPME fiber to the mass spectrometer. Mass fragmentation data resulting from the unresolved milk volatile components were subjected to MVA. Principal component analysis based on SPME-MS-MVA provided rapid differentiation of control reduced-fat milk (2% butterfat content) samples from reduced-fat milk samples abused by light, heat, copper, and microbial contamination. The three psychrotrophic bacteria studied included Pseudomonas fluorescens, Pseudomonas aerofaciens, and Pseudomonas putrefaciens. SPME-MS-MVA is rapid and offers significant advantages over commercial electronic nose instruments currently being used as quality assurance tools to differentiate normal-tasting food and beverage samples from those containing off-flavors and malodors.

(113) Similarities in the aroma chemistry of Gewurztraminer variety wines and lychee (Litchi chinesis Sonn.) fruit, Ong_PKC, Acree_TE, CORNELL UNIV,NEW YORK STATE AGR EXPT STN,DEPT FOOD SCI & TECHNOL, GENEVA, NY, 14456, JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY, 1999, Vol.47, No.2, pp.665-670. GC/O analysis of canned lychees indicated that cis-rose oxide, linalool, ethyl isohexanoate, geraniol, furaneol, vanillin, (E)-2-nonenal, beta-damascenone, isoalieric acid, and (E)-furan linalool oxide were the most odor potent compounds detected in the fruit extracts. However, on the basis of calculated odor activity values (OAVs), cis-rose oxide, beta-damascenone, linalool, furaneol, ethyl isobutyrate, (E)-2-nonenal, ethyl isohexanoate, geraniol, and delta-decalactone were determined to be
the main contributors of canned lychee aroma. When these results were compared with GC/O results of fresh lychees and Gewurztraminer wine, 12 common odor-active volatile compounds were found in all three products. These included cis-rose oxide, ethyl hexanoate/ethyl isohexanoate, beta-damascenone, linalool, ethyl isobutyrate, geraniol, ethyl 2-methylbutyrate, 2-phenylethanol, furaneol, vanillin, citronellol, and phenethyl acetate. On the basis of OAVs, cis-rose oxide had the highest values among the common odorants in the three products, indicating its importance to the aroma of both lychee fruit and Gewurztraminer wines. Other compounds that had significant OAVs included beta-damascenone, linalool, furaneol, ethyl hexanoate, and geraniol. This indicated that while differences exist in the aroma profile of lychee and Gewurztraminer, the common odorants detected in both fruit and wine, particularly cis-rose oxide were responsible for the lychee aroma in Gewurztraminer wine. When headspace SPME was used as a rapid analytical tool to detect the levels of selected aroma compounds deemed important to lychee aroma in Gewurztraminer-type wines, cis-rose oxide, linalool, and geraniol were found to be at relatively higher levels in Gewurztraminers. No cis-rose oxide was detected in the control wines (Chardonnay and Riesling), while lower levels were detected in the Gewurztraminer-hybrid wine Traminette. Gewurztraminers produced in the Alsace region showed differences in the levels of the 3 monoterpenes when compared to those from New York State, which could be attributed to differences in viticultural and enological practices between regions.

(114) Headspace solid-phase microextraction for the determination of benzene, toluene, ethylbenzene and xylenes in urine, Fustinoni_S, Giampiccolo_R, Pulvirenti_S, Buratti_M, Colombi_A, IST CLIN PERFEZIONAMENTO, VIA S BARNABA 8,I-20122 MILAN,ITALY UNIV MILAN,DIPARTIMENTO MED LAVORO,I-20122 MILAN,ITALY, JOURNAL OF CHROMATOGRAPHY B, 1999, Vol.723, No.1-2, pp.105-115. A method for the determination of benzene, toluene, ethylbenzene and xylenes (BTEX) in urine of people exposed to these airborne pollutants present in the living environment, has been described. Solid-phase microextraction has been used for sampling BTEX from the headspace of urine and gas chromatography-mass spectrometry has been applied for the selective analysis of chemicals. The method has the following features: small volume of urine (2 ml) needed, linearity in the range of interest (from the limit of detection up to 5000 ng/l) with coefficient of correlation greater than or equal to 0.998, limit of detection in the range 12-34 ng/l, good repeatability (coefficient of variation 2-7%), high specificity. The stability of the urine sample during storage (-20 degrees C) was evaluated: BTEX remained stable for up to 2 months. The assay has been successfully applied to the biological monitoring of two subjects environmentally exposed to airborne BTEX in an urban area.

polydimethylsiloxane and mixed Carboxen-polydimethylsiloxane SPME fibres were found to be suitable for the headspace extraction of TMA. This new sampling technique could have wide application for the analysis of volatile and semi-volatile compounds by metabolic screening laboratories.

(116) Slid-phase microextraction of volatile polar compounds in water, Matisova_E, Sedlakova_J, Slezackova_M, Welsch_T, SLOVAK TECH UNIV,FAC CHEM TECHNOL,DEPT ANALYT CHEM,RADLINSKEHO 9,BRATISLAVA 81237,SLOVAKIA UNIV ULM,D-89081 ULM,GERMANY, HRC-JOURNAL OF HIGH RESOLUTION CHROMATOGRAPHY, 1999, Vol.22, No.2, pp.109-115. A method was developed for the analysis of volatile polar compounds in a water matrix using open cap vials Solid Phase Micro-Extraction (SPME) and Capillary Gas Chromatography (CGC). Both SPME techniques - direct sampling and headspace - were tested. Optimization of experimental conditions - exposure time, desorption time, with headspace SPME in addition the influence of the temperature and ionic strength of the sample solution on compound sorption, and finally GC response - were investigated. The analytes were extracted by directly immersing the 85 μm polyacrylate fiber in the aqueous sample or in the headspace. The linear range of the preconcentration process and the precision were examined. The amount of polar analytes sorbed on the fiber was determined and was found to be concentration dependent; it amounted to 0.014-0.64% in the concentration range of 0.00425-425 ppm studied in aqueous solution for direct sampling SPME and to 0.011-2.76% for solutions of concentration 0.0425-255 ppm for headspace SPME. The limits of determination were ascertained. Headspace SPME was applied to the analysis of real-life samples.

(117) Automated determination of 'Ecstasy' and amphetamines in urine by SPME and capillary gas chromatography after propylchloroformate derivatisation, Ugland_HG, Krogh_M, Rasmussen KE, UNIV OSLO,INST PHARM,POB 1068 BLINDERN,N-1068 OSLO,NORWAY UNIV OSLO,INST PHARM,N-1068 OSLO,NORWAY, JOURNAL OF PHARMACEUTICAL AND BIOMEDICAL ANALYSIS, 1999, Vol.19, No.3-4, pp.463-475. The determination of amphetamines and their methylenedioxyylated analogs in urine by propylchloroformate derivatisation and automated solid-phase microextraction is described. The urine sample was adjusted to pH 10.8 and added propylchloroformate reagent and an internal standard. Derivatisation resulted in water-stable carbamates which were automatically extracted by solid-phase microextraction. A fiber coated with polydimethylsiloxane was inserted into the urine matrix and agitated for 16 min. The fibre with the extracted carbamates was injected into the heated split-splitless injection port of the gas chromatograph where the analytes were evaporated at 300 degrees C, separated on a methylsilicone capillary column and detected by either a nitrogen-phosphorous detector or by mass spectrometry. The method was shown to be highly reproducible and robust with respect to variations in the urine matrices. The detection limits were 5 ng ml(-1) of methamphetamine, MDMA and MDEA and 15 ng ml(-1) of amphetamine and MDA in urine. The method is a solvent free, automated alternative to traditional methods for determination of the amphetamine and their methylenedioxyylated analogs in urine.

(118) Method for analyzing urinary toluene and xylene by solid-phase microextraction (SPME), and its application to workers using organic solvents, Asakawa_F, Jitsunari_F, Choi_J, Suna_S, Takeda_N, Kitamado_T, KURASHIKI UNIV SCI & ARTS,COLL LIBERAL ARTS & SCI,HUMAN ENVIRONM SCI RES
Classification of wines by means of multivariate data analysis using the SPME/CGC-chromatograms of volatile aroma compounds, Garcia/DD, Reichenbacher_M, Danzer_K, UNIV JENA, INST ANORGAN & ANALYT CHEM, LESSINGSTR 8, D-07743 JENA, GERMANY, UNIV JENA, INST ANORGAN & ANALYT CHEM, D-07743 JENA, GERMANY, VITIS, 1998, Vol.37, No.4, pp.181-188.

The solid phase microextraction (SPME) is an effective solvent-free sample preparation technique for the capillary gas chromatographic (CGC) analysis of volatile aroma compounds of wines. Using discriminant analysis based upon only two terpene compounds, it was possible to analytically discern between the varieties Riesling, Muller-Thurgau and Silvaner grown in the same region. The discrimination of these varieties was unsuccessful for wines of different vintages (1988-1995). In order to obtain a highly significant classification, it was necessary to consider further aroma components described in wine literature. The differentiation between these wines by a similar high classification rate was obtained using a set of variables selected by mathematical methods. Wines prepared from known grape varieties were qualitatively recognized by factor-and cluster-analyses as well as the relative peak intensities of the terpene compounds in the SPME-CGC chromatograms. The composition of wine blends was quantitatively determined.


A simple and rapid method for the determination of benzene and toluene in whole blood by headspace-solid-phase microextraction (HS-SPME) is described. Using SPME fibres coated with 65 μm carboxene/polydimethylsiloxane, limits of quantification (LOQ) of 5 ng/L for benzene and 25 ng/L for toluene are achieved. As a result of its large linear range (i.e. 5-5000 ng/L for benzene) the method is suitable for biomonitoring of both occupationally and environmentally exposed people. The reproducibility of the determination of benzene is less than or equal to 8%. An interlaboratory comparison demonstrated that the method proposed here compares favorably with existing methods (dynamic headspace, purge and trap).


This paper describes the determination of Henry's law coefficients by means of the EPICS (equilibrium partitioning in closed systems) technique in combination with SPME (solid-phase microextraction). The use of solid-phase
Microextraction sampling allowed us to extend the possibilities of the equilibrium partitioning in closed systems technique with respect to the range of Henry's law coefficients which can be measured. Whereas the equilibrium partitioning in closed systems technique is limited to determine air-water equilibrium partitioning of volatile compounds with Henry's law coefficients of at least 0.06 (dimensionless), the current method allowed to measure coefficients between 0.0023 and 13.5. In this way Henry's law coefficients of 20 compounds, being in a range covering five orders of magnitude, were measured with relative standard deviations between 1.0 and 19.8% (mean standard deviation: 5.7%; median of standard deviations: 4.8%, n=99). Several types of compounds were examined i.e. aliphatic hydrocarbons, monocyclic and polycyclic aromatic hydrocarbons, chlorinated and fluorinated compounds, ethers and esters, biphenyl and N-containing compounds, including compounds for which availability of experimental Henry's law coefficients is limited. Measurement of the equilibrium partitioning in the 2 to 25 degrees C range allowed to establish relations of Henry's law coefficient as a function of temperature.

(122) Headspace solid phase microextraction (HSSPME) for the determination of volatile and semivolatile pollutants in soils. Llompart_M, Li_K, Fingas_M, UNIV SANTIAGO COMPOSTELA,FAC QUIM,DEPT QUIM ANALIT NUTR & BROMATOL,E-15706 SANTIAGO COMPOSTE,SPAIN ENVIRONM CANADA,ENVIRONM TECHNOL CTR,EMERGENCIES SCI DIV,OTTAWA,ON,CANADA, TALANTA, 1999, Vol.48, No.2, pp.451-459. We have investigated the use of headspace solid phase microextraction (HSSPME) as a sample concentration and preparation technique for the analysis of volatile and semivolatile pollutants in soil samples. Soil samples were suspended in solvent and the SPME fibre suspended in the headspace above the slurry. Finally, the fibre was desorbed in the Gas Chromatograph (GC) injection port and the analysis of the samples was carried out. Since the transfer of contaminants from the soil to the SPME fibre involves four separate phases (soil-solvent-headspace and fibre coating), parameters affecting the distribution of the analytes were investigated. Using a well-aged artificially spiked garden soil, different solvents (both organic and aqueous) were used to enhance the release of the contaminants from the solid matrix to the headspace. It was found that simple addition of water is adequate for the purpose of analysing the target volatile organic chemicals (VOCs) in soil. The addition of 1 ml of water to 1 g of soil yielded maximum response. Without water addition, the target VOCs were almost not released from the matrix and a poor response was observed. The effect of headspace volume on response as well as the addition of salt were also investigated. Comparison studies between conventional static headspace (IES) at high temperature (95 degrees C) and the new technology HSSPME at room temperature (similar to 20 degrees C) were performed. The results obtained with both techniques were in good agreement. HSSPME precision and linearity were found to be better than automated headspace method and HSSPME also produced a significant enhancement in response. The detection and quantification limits for the target VOCs in soils were in the sub-ng g(-1) level. Finally, we tried to extend the applicability of the method to the analysis of semivolatiles. For these studies, two natural soils contaminated with diesel fuel and wood preservative, as well as a standard urban dust contaminated with polycyclic hydrocarbons (PAHs) were tested. Discrimination in the response for the heaviest compounds studied was clearly observed, due to the poor partition in the headspace and to the slow kinetics of all the processes involved in HSSPME.
Direct solid-phase microextraction combined with gas and liquid chromatography for the determination of lidocaine in human urine, Koster_EHM, Hofman_NSK, deJong_GJ, UNIV GRONINGEN,CTR PHARM,DEPT ANALYT CHEM & TOXICOLO,A DEUSINGLAAN 1, NL-9713 AV GRONINGEN, NETHERLANDS, CHROMATOGRAPHIA, 1998, Vol.47, No.11-12, pp.678-684. Solid-phase microextraction (SPME) has been combined with gas chromatography (GC) and liquid chromatography (LC) for the determination of lidocaine in human urine. A polydimethylsiloxane (PDMS) coated fibre was directly immersed into buffered urine. Extraction conditions such as time, pH, ionic strength, temperature, and agitation were optimised. The extracted lidocaine was thermally desorbed in a split/splitless injector for analysis with a GC-FID system or desorbed with liquid in a specially designed SPME-LC interface for analysis with an LC-UV system. After optimisation the method developed was evaluated and validated. Extraction yields of 22% were obtained in about 45 min. The reproducibility of the method is < 5% (relative standard deviation). For five-times diluted urine, linear ranges were found from 5-1000 and 25-1000 ng.mL(-1) for SPME-GC and SPME-LC, with detection limits of 5 ng.mL(-1) for SPME-GC and 25 ng.mL(-1) for SPME-LC. SPME can be used as a simple sample pretreatment method for the determination of lidocaine in urine by GC and LC.

Analysis of 2-methylisoborneol and geosmin in catfish by microwave distillation-solid phase microextraction, Lloyd_SW, Grimm_CC, USDA ARS,SO REG RES CTR,1100 ROBERT F LEE BLVD,NEW ORLEANS, LA,70124, JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY, 1999, Vol.47, No.1, pp.164-169. The semivolatile cyclic alcohols 2-methylisoborneol (MIB) and geosmin (GSM) impart muddy or musty flavors to water and food products. A rapid quantitative analytical technique has been developed whereby microwave distillation is used to remove the volatile organic compounds from a lipophilic matrix into an aqueous matrix. Solid-phase microextraction (MD-SPME) is then used to extract and concentrate the analytes, which are then desorbed in the injection port of a gas chromatograph/mass spectrometer (GC/MS) for analysis. Limits of detection are 0.01 µg/kg and limits of quantification are 0.1 µg/kg. MD-SPME is comparable in precision, requires no solvents, and is faster than current methods of analysis; This methodology allows detection of MIB and GSM at concentrations below human sensory thresholds in fish tissue.

Determination of chlorobenzenes in environmental samples using solid phase microextraction, thermal desorption and analysis by gas chromatography coupled to FID, ECD, MSD IRD detectors, Takats_Z, Torkos_K, EOTVOS LORAND UNIV SCI,DEPT GEN & INORGAN CHEM, POB 32, H-1518 BUDAPEST 112,HUNGARY EOTVOS LORAND UNIV SCI,DEPT GEN & INORGAN CHEM,H-1518 BUDAPEST 112,HUNGARY, CHROMATOGRAPHIA, 1998, Vol.48, No.1-2, pp.74-80. A complex method was developed for the determination of chlorobenzenes in soil and groundwater samples. Samples were taken at two sites in Baranya county, where a mixture of chlorobenzene waste was deposited, causing severe contamination in the environment. Clean-up of these sites demands modern and reliable analytical methods. Several sample preparation techniques were used, such as solid phase microextraction (SPME), supercritical fluid extraction (SFE), and a recently developed thermal desorption method. The applicability of various sample preparation methods was compared by measuring recovery percentages, relative standard deviations and by
investigating the matrix dependency of these values. Gas chromatography was used for quantitative determination of chlorobenzenes, using MS, IR, FID and ECD detection techniques. Detection levels were as low as 1 ppt in water, and 10 ppt in soil samples. Chlorobenzene concentration was in the range 1 ppt-1 ppm in water and 100 ppb-100 ppm in soil samples. Identification and calibration of these compounds were performed by quantitative standards. This complex analytical method can be used for rapid and precise quantitative and qualitative determination of chlorobenzenes.

(126) Quantitative analysis of aliphatic aldehydes by headspace SPME sampling and ion-trap GC-MS, Keszler_A, Heberger_K, Gude_M, HUNGARIAN ACAD SCI,CENT RES INST CHEM,POB 17,H-1525 BUDAPEST, HUNGARY UNILEVER RES LABS VLAARDINGEN,NL-3130 AC VLAARDINGEN,NETHERLANDS, CHROMATOGRAPHIA, 1998, Vol.48, No.1-2, pp.127-132. A fast and simple headspace SPME sampling method has been developed for quantification of volatile aliphatic aldehydes in sunflower oil. Analysis has been performed by gas chromatography, on a 30 m x 0.25 mm i.d. x 0.25 μm CP-Wax 52CB column, with mass spectrometric detection. Carryover from the SPME fiber could be eliminated by heating the fiber in the injection port between runs. Response factors of all the compounds were linear for concentrations up to 100 ng μL-1. The slopes of the calibration curves decrease with the amount of saturation of the aldehydes. The average responses for unsaturated aldehydes were twice as high as those for the saturated variety. Responses for dienes were approximately one order of magnitude higher than for saturated aldehydes. Depletion of the analyte was examined by repeated extraction from the same vial. SPME was optimized - after 30 min extraction most components were found to have reached equilibration. The detection limit for the compounds studied varied between 0.1 and 1 ng μL-1. Distribution constants were determined for ten different aldehydes and Henry's constants were calculated for unsaturated aldehydes. There was a definite relationship between the response factors and the amount of saturation of the aldehydes.

(127) Determination of methylcyclopentadienylmanganese tricarbonyl (MMT) in aqueous samples by SPME-GC-AED, Yang_F, Chau_YK, ENVIRONM CANADA,CANADA CTR INLAND WATERS,NATL WATER RES INST,BURLINGTON,ON L7R 4A6,CANADA, ANALYST, 1999, Vol.124, No.1, pp.71-73. Solid phase microextraction (SPME) was successfully applied to the determination of the gasoline additive methyl cyclopentadienyl manganese tricarbonyl (MMT) in aqueous samples. The procedure is simple, efficient and solvent free. Ultra-trace levels of MMT (pg l(-1)) in water can be determined with the combination of SPME and gas chromatography-plasma atomic emission detection. The linear range is between 1 and 1000 pg l(-1) with relative detection limits of 0.3 pg l(-1) as Mn) of MMT in water. The precision for replicate analyses (n = 4) of an MMT solution (10 pg l(-1) as Mn) was 7.1% (RSD). Different kinds of aqueous samples were collected and extracted for the determination of MMT with the SPME technique. In spite of its short half-life in the presence of light, MMT was found in all highway runoff and effluent samples. The liquid-liquid extraction method was also used for MMT determination in highway runoff and lake water samples and the results from the two techniques were comparable.

(128) Solid-phase microextraction with pH adjustment for the determination of aromatic acids and bases in water, vanDoorn_H, Grabanski_CB, Miller_DJ,
Adjusting the pH of water samples before performing solid-phase microextraction (SPME) analysis can be used to selectively extract organic acids (at pH 2) and bases (at pH 12). Sorption behavior of test organics is predictable based on the acid dissociation constant in water. In general, polyacrylate (PA) and Carbowax-divinylbenzene (CW-DVB) show substantially higher fiber/water sorption coefficients (K-d, values) than a polydimethylsiloxane (PDMS) coated fiber. Gas chromatography-flame ionization detection (GC-FID) detection limits with the CW-DVB sorbent are similar to 0.5 to 10 ng/ml in a 2-ml water sample for a variety of aromatic amines, phenols, and chlorinated phenols, and are similar to 1 to 50 ng/ml for the same solutes using the PA sorbent. However, the PA fiber is more selective (depending on the water pH) for the acid or base components than the CW-DVB fiber. With proper pH adjustment, the recovery of spiked aromatic amines and phenols from a surface wetlands water ranged from 73 to 118% of the known values, with a precision (R.S.D.) of similar to 5 to 20%. SPME quantitation of phenols in a coal gasification wastewater using a PA fiber also gave excellent agreement with conventional methylene chloride extraction, although continued use of a single fiber with this wastewater led to poorer precision.

Solid-phase microextraction coupled with high-performance liquid chromatography (SPME-HPLC) and fluorescence detection was used to determine an alcohol ethoxylate (Brij 56) and 1-hexadecanol in water samples. Determinations were achieved by extraction with polydimethylsiloxane-divinylbenzene (PDMS-DVB) SPME fibers and pre-column derivatization with 1-naphthoyl chloride in the presence of 4-(dimethylamino)pyridine (DMAP) as catalyst. Variables such as time of reaction and concentration of surfactant in water were evaluated. The limit of detection of the method was found to be 0.1 mg/l of Brij 56.

Solid-phase microextraction (SPME) has been applied to the residual solvents determination in pharmaceutical products and was compared with the static headspace. Three fibers with different polymer films were compared and the polydimethylsiloxane/divinylbenzene coated fiber was found to be the most sensitive for the analyzed analytes. Between the investigated sample preparation techniques, gastight-SPME proved to be the most sensitive, with DL values ranging from 5 pg ml(-1) to 2 ng ml(-1). Headspace SPME is more precise, with RSD of peak areas values ranging from 2 to 3%. The headspace SPME method was successfully validated. The validation data are reported in the text. The most important difference between the two techniques is that the gastight SPME
showed better behavior towards very volatile solvents. Compared with the static headspace technique, both SPME methods showed superior results, being compatible with the pharmaceutical samples.

(131) Determination of benzodiazepines in human urine and plasma with solvent modified solid phase micro extraction and gas chromatography; rationalisation of method development using experimental design strategies, Reubsaat_KJ, Norli_HR, Hemmersbach_P, Rasmussen_KE, UNIV OSLO,SCH PHARM,POB 1068 BLINDERN,N-0316 OSLO,NORWAY AKER HOSP,HORMONE LAB,N-0514 OSLO,NORWAY, JOURNAL OF PHARMACEUTICAL AND BIOMEDICAL ANALYSIS, 1998, Vol.18, No.4-5, pp.667-680. Solid phase micro extraction (SPME) and gas chromatographic analysis was used for the analysis of several benzodiazepines (oxazepam, diazepam, nordiazepam, flunitrazepam and alprazolam) in human urine and plasma. Several factors likely to affect the analyte recovery were screened in a fractional factorial design in order to examine their effect on the extraction recovery. Parameters found significant in the screening were further investigated with the use of response surface methodology. The final conditions for extraction of benzodiazepines were as follows: Octanol was immobilised on a polyacrylate fibre for 4 min. The fibre was placed in the sample and extraction took place at pH 6.0 for 15 min. Urine samples were added to 0.3 g ml(–1) sodium chloride. In plasma, the extraction recovery was less than in urine and releasing the benzodiazepines from plasma proteins followed by protein precipitation was found necessary prior to sampling. The method was validated and found linear over the range of samples. The limits of detection in urine were determined to be in the range 0.01-0.45 μmol l(–1). The corresponding limits of detection in plasma were in the range 0.01-0.48 μmol l(–1). Finally, the method developed was applied to determine some benzodiazepines after administration of a single dose. This method offer sufficient enrichment for bioanalysis after a single dose of high dose benzodiazepines as diazepam, but for low dose benzodiazepines as flunitrazepam, further sensitivity is needed.


(133) Volatiles attractive to the Mexican fruit fly (Diptera: Tephritidae) from eleven bacteria taxa, Robacker_DC, Martinez_AJ, GarciaJA, Bartelt_RJ, USDA ARS,2301 S INT BLVDA,WESLACO,TX,76259 USA, MISSION BIOL CONTROL CTR,ANIM & PLANT HLTH INSPECT SERV,MISSION,TX,78573 USA ARS, NATL CTR AGR UTILIZAT RES,PEORIA,IL,61604, FLORIDA ENTOMOLOGIST, 1998, Vol.81, No.4, pp.497-508. Filtrates of 11 bacteria representing 4 higher taxonomic categories were attractive to Mexican fruit flies, Anastrepha ludens (Loew) (Diptera: Tephritidae) in laboratory bioassays. All bacterial filtrates were more attractive at pH 9 than at pH 5 although filtrates at pH 5 were more attractive than water controls. The effects of pH on attractiveness of filtrates were consistent with an hypothesis that attractive principals of
bacterial filtrates were various nitrogen-containing compounds and carboxylic acids that became more volatile at specific pH's resulting in increased attractiveness. Volatiles produced by the bacteria were sampled by solid-phase microextraction and identified by GC and CC-MS. Attractive principals identified were ammonia, aliphatic amines, pyrazines, imines, and acetic acid. Relative amounts of most of the chemicals were not closely tied to bacteria taxonomy.

(134) Comparison of gas-sampled and SPME-Sampled static headspace for the determination of volatile flavor components, Miller_ME, Stuart_JD, UNIV CONNECTICUT, DEPT CHEM, U-60, 55 N EAGLEVILLE RD, STORRS, CT, 06269 UNIV CONNECTICUT, DEPT CHEM, STORRS, CT, 06269, ANALYTICAL CHEMISTRY, 1999, Vol.71, No.1, pp.23-27. I Traditional static headspace and headspace solid-phase microextraction (SPME) techniques were compared for their effectiveness in the extraction of volatile flavor compounds from the headspace of various juice samples; Each method was used to evaluate the responses of certain analytes from real samples and calibration standards in order to provide sensitivity comparisons between the two techniques. Experimental results showed traditional static headspace lacked the sensitivity needed to evaluate certain flavor volatiles, such as alpha-terpinene and linalool, and that further concentration of the headspace was necessary. Dramatic improvements in the extraction abilities of the SPME fibers over the traditional static headspace method were noted. Different SPME fibers were investigated to determine the selectivities of the various fibers to the different flavor compounds present in the juice samples. Of the various fibers investigated, the PDMS/DVB fiber proved to be the most useful for these analyses. Aging studies of juice samples were also performed which verified that degradation could be observed and quantified.

(135) Nonequilibrium quantitation of volatiles in air streams by solid-phase microextraction, Bartelt_RJ, Zilkowski_BW, USDA ARS, NATL CTR AGR UTILIZAT RES, BIOACT AGENTS RES UNIT, 1815 N UNIV ST, PEORIA, IL, 61604, ANALYTICAL CHEMISTRY, 1999, Vol.71, No.1, pp.92-101. Solid-phase microextraction (SPME) is a valuable technique for analyzing air-borne organic compounds; one important application is measuring concentrations when these are constant over time. Quantitation normally relies on the SPME fiber being fully equilibrated with the sample medium. Unfortunately, relatively heavy compounds do not equilibrate within a reasonable amount of time, and this has limited the scope of SPME. The ability to quantitate during equilibration was needed and was the focus of this investigation. This entailed having an accurate description of SPME kinetics, and the kinetics of extraction by poly(dimethylsiloxane) fibers was studied for alkanes of 9-22 carbons, primary alcohols of 6-13 carbons, and methyl esters of 6-16-carbon acids. Sampling was from air streams in which analyte concentrations were effectively constant, and sampling times ranged from 30 min to 3 days. Other experimental variables included sampling temperature, fiber coating thickness, air flow rate, and tubing diameter in which the SPME sampling took place. Over 1900 data points were acquired. Previous theoretical kinetic models were not applicable to the present experimental conditions, but a simple kinetic equation was formulated that described the data very well; its key property is an explicit relationship between fiber sensitivity and equilibration time. Using nonlinear regression, the equation parameters were linked to known properties of the analyte (the functional group and GC retention index on a nonpolar column) and to certain sampling conditions (temperature, sampling duration,
air now rate, tubing diameter). The regression equation serves as a practical quantitation
formula and allows the absolute concentration of the analyte in the air stream to be
calculated directly from the amount extracted by the SPME fiber (which is easily
measured by GC), regardless of whether equilibrium has been established or not, as
long as the above analyte properties and sampling conditions are known. The residual
variability for the model (RSD = 9.4%) was only slightly larger than the variability
inherent in SPME alone (similar to 5%). Considerations for SPME sampling from air are
discussed, and new fiber calibration information is presented for the larger
hydrocarbons, alcohols, and methyl esters.

(135) Solid phase micro extraction coupled with semi-microcolumn high performance
liquid chromatography for the analysis of benzodiazepines in human urine, Jinno_K,
Taniguchi_M, Hayashida_M, TOYOHASHI UNIV TECHNOLOG.SCH MAT
SCI,TOYOHASHI, AICHI 4418580, JAPAN NIPPON MED COLL, DEPT LEGAL
MED, TOKYO 1130022, JAPAN, JOURNAL OF PHARMACEUTICAL AND
BIOMEDICAL ANALYSIS, 1998, Vol.17, No.6-7, pp.1081-1091.: SPME/semi-
microcolumn HPLC (SPME/LC) was investigated to analyze benzodiazepines in human
urine samples. SPME conditions such as extraction time, extraction temperature, salt
concentration and pH of matrix, flush volume and desorption time were optimized by
extracting various drugs from a prepared water matrix. Combination of adding
saturated salts to the matrix and controlling pH ranged from neutral to weakly alkaline
conditions makes the increase of extraction efficiency. Under optimal condition
SPME/LC is more sensitive than direct HPLC analysis without the SPME process. The
limits of detection (LODs) was several ppb level and the relative standard deviation
(RSD) was < 15% when human urine samples were analyzed by this analytical system.
The system is very useful and is enough to assay benzodiazepines in a human urine
sample without tedious and complex analytical procedures. In this paper the
applicability of SPME/LC to the analysis of benzodiazepines in human urine samples
was reported. In addition, the extension to the evaluation of SPME/LC/IMS system was
also described.

(137) Chemical and morphological changes of environmentally degradable
polyethylene films exposed to thermo-oxidation. Khabbaz_F, Albertsson_AC,
Karlsson_S, ROYAL INST TECHNOL, DEPT POLYMER TECHNOLOG.S-10044
STOCKHOLM, SWEDEN, POLYMER DEGRADATION AND STABILITY, 1999,
Vol.63, No.1, pp.127-138.: Thermo-oxidation of blown low density polyethylene
(LDPE) films modified with different combination of biodegradable filler, prooxidant
and photosensitizers was conducted in oven at 60 and 100 degrees C for a period of 14
days. Volatile and semivolatile degradation products were extracted by solid phase
micro extraction (SPME) technique and identified utilizing gas chromatography-mass
spectrometry (GC-MS). Chemical and morphological changes were monitored and
these are given as carbonyl index, crystallinity and melting behavior, molecular weight
and molecular weight distribution. The samples containing solely prooxidant showed
the highest susceptibility to thermal degradation during the test period. The second most
degradable samples were LDPE modified with 20% masterbatch (containing starch and
a prooxidant). LDPE containing only starch did not show any degradation during the
test period. The major degradation products were homologous series of carboxylic
acids, ketones, hydrocarbons and lactones. 4-Oxopentanoic acid, 5-oxohexanoic acid
and benzoic acid were identified only in LDPE containing prooxidant (LDPE-PO) and
LDPE modified with 20% masterbatch (LDPE-MB). A small number of aldehydes (3-
methyl pentanal, benzaldehyde and 2-propyl 5-oxohexanal) were identified solely in LDPE-MB. Esters could be identified only from LDPE-Starch and pure-LDPE samples. The crystallinity of all the samples increased after aging at 60 degrees C except for LDPE-Starch which showed no significant change in crystallinity. The melting thermograms of LDPE-PO and LDPE-MB (first heating) exhibited low temperature shoulders around 75 degrees C (after treatment at 60 degrees C) and appears to move downward with increasing exposure temperature (treatment at 100 degrees C). The shoulders near 115 degrees C (second heating) increase with increasing exposure temperature which is due to a preferential scission at the tertiary carbon atom as observed by increased crystalline melting point. ATR and transmission FTIR show that the absorbance of carbonyl containing groups is almost the same on the surface as in the bulk for virgin samples and samples aged at 60 degrees C. Opposite to the other materials, LDPE-MB samples aged at 100 degrees C show a much faster increase in the absorbance of carbonyl containing groups in the bulk of the film than on the surface layer. This indicates that the bulk of the latter films are more labile than the surface which could be a consequence of higher starch concentration on the surface than in the bulk.

(138) Analysis of volatile fatty acids in wastewater collected from a pig farm by a solid phase microextraction method, Yo_SP, NATL CHUNGHISING UNIV, DEPT ZOOL, 250 KUO KUANG RD, TAICHUNG 402, TAIWAN, CHEMOSPHERE, 1999, Vol. 38, No.4, pp. 823-834. The main purpose of this study is to develop a reliable Solid Phase Microextraction (SPME) method for monitoring the concentration of volatile fatty acid (VFA) in the wastewater collected from pig farms. Ten volatile fatty acid species were spiked in 2 ml of swine wastewater and extracted with a carbowax coated extraction fiber to evaluate the accuracy and precision of the method. The fiber was introduced into a gas chromatography system by thermal desorption and detected by a mass spectrometer detector. The estimated method detection limits ranged from 11.5 mM/L for formic acid to 0.03 mM/L for heptanoic acid. The method is more sensitive than the sample direct injection method. The percentage recovery of analytes ranged from 77.3 for propanoic acid to 114.1 for formic acid at the spike level of 19.09 mM/L. The compound absorption rate varied significantly with the fiber absorption time for n-Valeric, isocaproic, n-caproic and heptanoic acids. An SPME method with twenty minutes fiber absorption and three minutes thermal desorption was tested in this study and resulted in good reproducibility for analyzing VFAs in swine wastewater. The method may be applied for scanning a wide spectrum of polar organic compounds in environmental samples.

(139) The effect of sample volume on quantitative analysis by solid phase microextraction - Part 2. Experimental verification Gorecki_T, Khaled_A, Pawliszyn_J, UNIV WATERLOO, DEPT CHEM, WATERLOO, ON N2L 3G1, CANADA, ANALYST, 1998, Vol. 123, No.12, pp. 2819-2824. The sample volume plays a very important role in solid phase microextraction (SPME) analysis. Its effect on the results of analysis can be neglected only when it is much larger than the fibre capacity KVf (K = fibre/sample partition coefficient, V-f fibre volume). Good agreement was obtained between theoretical predictions and experimental results for analyte extraction from two- and three-phase systems. The effect of headspace capacity on SPME extraction results and kinetics was illustrated on an example of amphetamine and methamphetamine determination in water. A dramatic improvement in extraction speed was achieved by increasing the extraction temperature, and thus also the headspace-
sample partition coefficients. Difficulties with the accurate determination of large partition coefficients are discussed on an example of the extraction of C-8-C-12 hydrocarbons from air. Analyte sorption on the container walls led to significant losses of less volatile compounds, especially when vials of large surface-to-volume ratio were used. A discussion of problems encountered when trying to determine accurately partition coefficients of semi-volatile compounds in water is also presented.

(140) Solid phase microextraction coupled to gas chromatography mass spectrometry for the determination of the adsorption coefficients of triazines in soil, Zambonin_CG, Catucci_F, Palmisano_F, UNIV BASILICATA,DIPARTIMENTO CHIM,VIA N SAURO 85,I-85100 POTENZA,ITALY UNIV BARI,DIPARTIMENTO CHIM,I-70126 BARI,ITALY, ANALYST, 1998, Vol.123, No.12, pp.2825-2828, Solid phase microextraction coupled to gas chromatography-mass spectrometry (SPME-GC-MS) was used to determine the adsorption coefficients (K-oc) for six target triazines in soil and sediment samples with different organic matter contents and textures. SPME-GC-MS was used in conjunction with a conventional batch equilibrium method. The recoveries of the selected triazines from soils and sediments having organic carbon contents in the range 0.2-2.4% were satisfactory. Drawbacks of conventional analytical techniques are avoided; owing to the selectivity of SPME-GC-MS, no sample pre-treatment or solvent enrichment steps were required so that K-oc values could be easily determined. Moreover, the sensitivity of the technique makes it possible to work at low triazine concentrations (50-500 ng g(-1)) where the Freundlich adsorption isotherm can be considered linear.

(141) Determination of benzene, toluene, ethylbenzene and xylenes in indoor air at environmental levels using diffusive samplers in combination with headspace solid-phase microextraction and high-resolution gas chromatography-flame ionization detection, Elke_K, Jermann_E, Begerow_J, Dunemann_L, MED INST UMWELTHYG,DEPT ANALYT CHEM,HENNEKAMP 50,D-40225 DUSSELDORF,GERMANY MED INST UMWELTHYG,DEPT ANALYT CHEM,D-40225 DUSSELDORF,GERMANY, JOURNAL OF CHROMATOGRAPHY A, 1998, Vol.826, No.2, pp.191-200. An improved analytical method for passive air sampling is presented based on a combination of commercially available diffusive samplers with headspace solid-phase microextraction and high-resolution gas chromatography with flame ionization detection (HRGC-FID). This procedure is targeted for short-term BTEX (benzene, toluene, ethylbenzene and o-, m- and p-xylenes) determinations at environmental concentrations and can be applied for sampling intervals between 30 min and 24 h. The analytes are adsorbed onto the charcoal pad of a passive sampler and then extracted with carbon disulphide-methanol. After removal of the carbon disulphide by xanthation, the BTEXs are enriched on a Carboxen SPME fiber, thermally desorbed and analysed by HRGC-FID. Detection limits for a sampling interval of 2 h are between 0.4 and 2 mu g/m3, within-series precision ranges between 6.6 and 12.8%, day-to-day precision is between 11.1 and 15.2%. The results obtained with this procedure are validated by comparison with active sampling. Detection limits and a further reduction of the sampling time are limited by blanks of the chemicals and the diffusive samplers. Procedures to eliminate these blanks are described in detail. Applications such as the determination of BTEXs in indoor air inside buildings, inside a train and a car are presented, indicating the usefulness of the described procedure for short-term measurements of environmental BTEX concentrations. An advantage of passive
samplers is the storage stability for at least six months, which is essential for its use in large epidemiological studies.