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Multiclass/multiresidue method for monitoring widely applied plant protecting agents in air during field dispersion work

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Abstract

A multiclass/multiresidue method for surveying the uptake of plant protecting chemicals by inhalation during field spraying work is described. Eleven nowadays mainly dispersed compounds, which cover a wide range of chemical properties, are analysed in air with personal active sampling and in one single analytical run. This has the advantage, that one basic method only needs to be implemented, calibrated and validated in a laboratory to perform varying monitoring tasks without changing the method itself. Samples were taken with Tenax sorbent tubes operated to collect the active compounds simultaneously in the vapour state, in aerosol state or bound to particles. The procedure consists of four unit operations only: sampling, elution, dilution and HPLC measurement, and is described in SOP-format. The limits of quantification, calculated as method detection limits, were between 1 and 9 $\mu g\ m^{-3}$ based on 1 m^3 air volume sampled (8 h). Method performance was characterised by way of generated test atmospheres and field spraying trials.

Keywords: Air analysis; Multiresidue methods; Plant-protecting agents; Pesticides

1. Introduction

Plant protectants are workplace substances which are potentially harmful for persons occupied in agriculture and forestry. Analytical methods are required for measuring their concentrations in air in order to monitor inhalatoric exposure of persons working with these agents, particularly in agriculture, during field distribution work in progress and all related handling.

Records of maximum concentrations of hazardous chemicals in workplace air and collections of recommended analytical procedures for their determination [1,2] are by no means complete with regard to plant protectant compounds, in particular considering the great number of active substances on the market today. If additional active compounds are to be included into those records, in particular newly registered ones, the capability to monitor them in air should also be accounted for in order to promote the acceptance and observation of limiting values.

Any new analytical procedure for this purpose should be designed as a true multiclass–multicompound method. The farmer bears a personal air sampling system mounted near the inhalation region, which is in operation during spraying work is in

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progress. Two reasons can be given for the multicompound approach: firstly, more than just one analyte must be expected in each air sample taken due to combination preparations, formulation additives and home-made mixtures. The other reason follows from analytical economy: it often happens, that persons dealing with rather different agrochemicals are to be monitored within one sampling series. It would be a great advantage if all samples delivered to the laboratory could be processed employing just one single basic method, which needs to be implemented, calibrated and validated only once.

The great number of preparations for sale makes it necessary to select those active compounds as target analytes, which are nowadays distributed in large amounts over the agricultural acreage of a defined area. For this study we selected the Austrian–Bavarian foothills of the Alps as geographic area and grain, maize and rape cultivation as agricultural mode of interest. This information is not accessible in the literature and had to be obtained from experts and users having knowledge of the plant protection practices in the respective region. The result of these consultations is a priority list of most popular plant protecting chemicals, which are also expected to be dispersed in even higher amounts within the next years (Table 1). The analytical task is to design a true multicompound method to identify and quantitate them at trace level in air, although they have rather different physicochemical properties and chemical reactivities. The method should be attractive for laboratories doing routine monitoring: it should be fast and simple, able to cope with differing measurement requirements, not prone to errors and moderate in costs.

Few articles are found up to now that describe sampling and analysis of trace plant protectants in ambient [5–8] and greenhouse air [9–12]. Most of the methods reported are designed for one or a few compounds only and do not employ personal sampling. A multiresidue method for urea herbicides is contained in the DFG method collection for air analysis [2]. A method designed for different chemical groups was reported by Sanusi et al. [13], however, this procedure involves a stationary high volume sampler and a rather tedious operation.

High-performance liquid chromatography (HPLC) with a pH gradient can be expected to provide the

Table 1
Priority list of plant protectant compounds investigated, some important properties and typical sales products

	pK_a	Water solubility (g l^{-1})	Vapour pressure (Pa)	Detection λ (nm)	Acceptable daily intake (ADI) (mg kg^{-1} d^{-1})	Typical sales products
Phenoxyalcanoic acids						
Dicamba	1.87, 1.97	6.5	$4.5\cdot10^{-3}$	210	0.0125	Banvel, Rumexan
Mecoprop, MCPP	3.40	0.7	$3.1\cdot10^{-4}$	226	0.0025	Duplosan, Hedonal
Sulfonylureas						
Thifensulfuron-methyl	4.0	6.3	$1.7\cdot10^{-8}$	226	0.026, 0.0125	Harmony
Metsulfuron-methyl	3.3	2.8	$3.3\cdot10^{-10}$	226	0.013	Ally, Concert
Dinitroaniline						
Pendimethalin		$3.0\cdot10^{-4}$	$4.0\cdot10^{-3}$	240	0.005	Stomp
Phenyl urea						
Isoproturon		$6.5\cdot10^{-2}$	$3.3\cdot10^{-6}$	240	0.0062, 0.0025	Alon, Tolkan, Graminon
N-Aryl carbamate						
Phenmedipham		$4.5\cdot10^{-3}$, $4.7\cdot10^{-3}$	$1.3\cdot10^{-9}$	210	0.03, 0.02	Betanal
Azole fungicides						
Propiconazole	1.09*	0.1	$5.6\cdot10^{-5}$	210	0.04, 0.02	Tilt
Prochloraz	3.8*	$3.4\cdot10^{-2}$	$1.5\cdot10^{-4}$	210	0.01	Sportak
Pyrethroides						
Cypermethrin		$4\cdot10^{-6}$	$2.3\cdot10^{-7}$	210	0.05	Cymbigon, Arpan
Deltamethrin		$2\cdot10^{-7}$	$1.3\cdot10^{-5}$	210	0.01	Decis

*pK_a of the protonated base. Data from Refs. [3,4].

selectivity, which is required to separate the analytes in one single run in view of their pK_a values. The vapour pressures indicate, that the compounds will be present primarily in the aerosol state or adsorbed on airborne particles, and only minor amounts in the vapour state. The suitability of Tenax as sorbent medium for this type of analytes is addressed in the literature [2,14]. A linear air flow-rate of 1.25 m s^{-1}, adjusted at the inlet of the collecting tube, assures the simultaneous quantitative sampling of vapourous analytes as well as all inhalable particles. Sampling efficiency is evaluated by adsorption from a generated test atmosphere simulating the environment encountered at field conditions. The design of a spray chamber to generate particulate material of a defined distribution of aerodynamic diameters is also described [14] and will be adopted here for method evaluation.

An important aspect was to design the analytical procedure to be straightforward and convenient. In particular evaporation and solvent exchange steps were avoided because they are time consuming and may increase the risk of losses and errors. Hence the objective was to realise an approach consisting of four basic unit operations only: sampling – elution – dilution – measurement.

The complete method is validated and evaluated in practical field spraying tests following the most important aspects of the NIOSH guidelines for air sampling and analytical development [15] and also the recommendations given in Ref. [16].

2. Experimental

2.1. Reagents and chemicals

Pesticide pure substances were purchased from Riedel-de Haen, except thifensulfuron-methyl and metsulfuron-methyl, which were purchased from DuPont. Purities were between 96 and 99%. Phenacetin Ph.Eur. (Merck) was used as internal standard substance.

Ammonium acetate of analytical-reagent grade, acetic acid 100% of analytical-reagent grade, hydrochloric acid solution, 0.1 mol l^{-1}, ammonia solution 25%, suprapur, and acetone of analytical-reagent grade were all obtained from Merck. Acetonitrile (MeCN), gradient grade quality, and methanol, residue analysis grade quality, were from Baker.

NH_3 solution, 0.1 mol l^{-1}, was prepared freshly before use.

Calibration buffer solutions, pH 3, 4 and 7, were prepared from Titrisol concentrates, Merck.

Helium 4.6 for degassing was obtained from Linde.

2.2. Solutions

2.2.1. HPLC eluents

Water of HPLC grade quality was exclusively used for all eluent preparations.

Eluent A: NH_4Ac buffer, 1 mmol l^{-1}, pH 4 – acetic acid solution, 1 mmol l^{-1}, was prepared and titrated to pH 4.0±0.05 with NH_3 solution, 0.1 mol l^{-1}, using a pH meter.

Eluent B: NH_4Ac buffer, 1 mmol l^{-1}, pH 6 – NH_4Ac solution, 1 mmol l^{-1}, was prepared and titrated to pH 6.0±0.1 with HCl solution, 0.1 mol l^{-1}, using a pH meter.

A 100-ml volume of acetonitrile was added to 900 ml of both buffer solutions to avoid microorganism growth. However, the eluents should be prepared freshly every 4 weeks.

Helium flow for degassing should be not higher than 5–10 ml min^{-1} because acetonitrile is blown-off gradually leading to a shift of the retention times.

2.2.2. Stock solutions

Single analyte stock solutions, 1 mg ml^{-1}, were prepared by dissolving 10±1 mg (recorded to nearest 0.1 mg) of each pure substance in 10 ml of MeCN–water solvent mixtures (volume-% compositions): dicamba, mecoprop (20:80); propiconazole (30:70); pendimethalin, isoproturon, cypermethrin (50:50); deltamethrin (70:30). Thifensulfuron-methyl, metsulfuron-methyl and phenmedipham were dissolved in pure MeCN, prochloraz in MeCN–NH_4Ac, 1 mmol l^{-1} (30:70). Stability was about 4 months when stored at +4°C.

The internal standard (I.S.) solution, 200 μg ml^{-1}, was prepared by dissolving 10±1 mg (recorded to nearest 0.1 mg) phenacetin in 50 ml methanol–water (20:80). Stability at room temperature was more than 4 months.

2.2.3. Working calibration solutions

Five composite working calibration solutions – 1, 5, 10, 25 and 50 μg ml^{-1} of each analyte – were prepared for working out the separation parameters, for linearity tests and design of the optimum calibration procedure for routine analysis: at first the most concentrated calibration solution was prepared by pipetting 2.50 ml of each stock solution into one 50-ml measuring flask and filling to volume with methanol–eluent B (1:1). The other calibration solutions were prepared by further dilution with methanol–eluent B (1:1).

For routine I.S. calibration two composite working calibration solutions – 2 and 10 μg ml^{-1} of each analyte with 5 μg ml^{-1} I.S. – were prepared: 400 μl and 2.00 ml, respectively, of the 50 μg ml^{-1} working calibration solution were pipetted into 10-ml volumetric flasks, 250 μl I.S. solution added to each and made up with methanol–eluent B (1:1).

2.2.4. Spiking solution

A composite spiking solution in acetone – 1 mg ml^{-1} of each analyte – was prepared: 25±2 mg (recorded to nearest 0.1 mg) of each pure substance were weighed into one 25-ml volumetric flask and made up with acetone.

2.3. Laboratory apparatus and materials

The following equipment was used: a semimicrobalance, capable of reading 0.1 mg – Mettler AT 261 Delta Range, an ultrasonic bath – Bandelin Sonorex RK510, a pH meter, capable of reading 0.01 pH – Metrohm 654 pH meter with single rod electrode, water purification equipment, capable of producing HPLC-grade quality water – Millipore Elix 3+Milli Q-plus 185 and a syringe filter attachment – Sartorius Minisart hydrophil 0.45 μm.

2.4. Field sampling equipment and procedure

2.4.1. Equipment

The following equipment was used: a portable air sampling pump with rechargeable battery, capable of maintaining a volumetric flow of 2 l min^{-1} over at least 8 h and automatic adjustment to correct for varying flow resistances – Buck S.S. Air Sampling Pump from A.P. Buck (Orlando, FL, USA), sampling tubes, Type NIOSH, 10 cm×6 mm I.D., containing 100 mg Tenax, 35–60 mesh, as sampling layer and 50 mg as backup layer with front, end and intermediate glass wool plugs – GK 26-35-03 GO from Günther Karl OHG (Germany) and a rotameter, range 0.6–5 l min^{-1} from CT Platon.

2.4.2. Sampling conditions

The sample holder was mounted horizontally in the respiratory region of the proband. Volumetric air flow was adjusted to maintain a linear flow velocity of 1.25 m s^{-1} ±10% at the inlet of the sampling tube, which means 2.1 l min^{-1}. The volumetric flow was calibrated before field sampling with the tube attached to the pump by using a rotameter.

Note: A trivial as well as frequent cause for erroneous results is an undetected leakage between sorbent pump and tube. It is extremely important to check the tightness of all connecting parts.

2.5. Elution and sample preparation

Tenax sampling and backup layer including the glass wool plugs were expelled from the collecting tube into separate 10-ml round bottom flasks and worked up individually. Front and intermediate glass wool plugs were added to the sampling layer, the end plug to the backup layer. A 5-ml volume of methanol was added through the empty tube followed by 5 min incubation with occasional shaking and subsequently 3 min ultrasonication. After sedimentation exactly 1 ml was taken from the supernatant through a 0.45-μm glass fibre filter attachment using a syringe, and placed into a 2-ml volumetric flask, 50 μl I.S. solution was added and filled to volume with water; this solution was ready for HPLC. If required the backup section was processed equally, although with 2.5 ml methanol.

2.6. HPLC measurement

The HPLC equipment used consisted of a Waters 590 LC system with a Waters 991 diode array detector and a Waters 717 autosampler. Analytical column: 250×4 mm LiChrospher 100 RP-18ec, 5 μm; pre-column: 4×4 mm LiChrospher 100 RP-18ec, 5 μm, both from Merck. Injection volume: 10 μl. Eluent flow: 1 ml min^{-1}. Detection wavelengths

Table 2
HPLC gradient

Time (min)	NH_4Ac buffer, pH 4 (%)	NH_4Ac buffer, pH 6 (%)	MeCN (%)
0	0	95	5
12	0	80	20
17	0	65	35
25	41	0	59
32	20	0	80
45	20	0	80
50	0	95	5

30 min equilibration.

for routine measurements are collected in Table 1. The ternary HPLC eluent gradient is given in Table 2.

2.7. Calibration and data evaluation

For routine measurements a two-point I.S. calibration procedure using the 2 and 10 μg ml^{-1} composite working calibration solutions (Section 2.2.3) is adequate. This covers a working range up to 100 μg m^{-3} based on an 8 h sampling time. Calibration solutions were injected in duplicate. The average relative response factors for each concentration, calculated from peak areas, should not deviate from the total average response factor by more than ±3%. A control calibration should be made after every 10 sample injections.

2.8. Recovery experiments

2.8.1. Spiking of sorbent tubes

For elution recoveries five tubes were spiked by injecting appropriate volumes of the spiking solution directly onto the Tenax layer with a gentle (~0.5 l min^{-1}) air flow to evaporate the solvent. Air was passed through subsequently with 2 l min^{-1} for 1 h. This corresponds to air concentrations between 0.2 and 2 mg m^{-3} on basis of a 1 h sampling time with 2 l min^{-1}.

For the determination of the method detection limits (MDLs) seven tubes were spiked in parallel, each with 100 μl of a specific spiking solution. The concentrations of the analytes in this spiking solution were matched to their individual detection sensitivity estimated previously from the S/N ratios in the chromatograms. Amounts were between 15 to 70 μg per compound and tube.

Spiking solutions from selected sales products (marked in Table 1) were prepared in acetone or acetone–water mixtures for water-soluble preparations. Since the contents of active ingredients (a.i.) were rather different the concentrations had to be chosen in such a way, that for each product two tubes could be spiked with absolute amounts corresponding to ~20 and ~200 μg a.i., respectively.

2.8.2. Generation of a test atmosphere

A standard solution was sprayed from the bottom into a spray chamber forming an aerosol–vapour atmosphere inside, which could exit through an side-arm port on top. This atmosphere was drawn through a Tenax sampling tube fed through this port together with a thermocouple. Sampling equipment and conditions were the same as used for monitoring and are described in Sections 2.4.1 and 2.4.2.

Spray chamber: a 10-l glass bottle with side-arm port, mounted bottom-up inside a drying oven.

Pneumatic spray nozzle: brass, 0.8 mm orifice for liquid delivery and 2.4 mm orifice for air flow – Model 970/0S3, Schlick (Germany).

Standard solution delivery: syringe pump – Harvard Apparatus 22.

Air delivery: compressed air supply, air filter – CompAir, rotameter with needle valve and differential pressure meter – Model RAGL41, Yokogawa (Japan).

Temperature measurement: multimeter BBC MA5D with temperature adapter Luton DH-802C and PT-100 thermocouple.

Aqueous standard solution – 10 μg ml of each compound investigated – containing 5% isopropanol.

Experimental conditions: air flow, reduced to standard state: 16.6 l min^{-1} (1 m^3 h^{-1}); solution flow: 0.5 ml min^{-1}; temperature: 35±2°C inside the spray chamber; time: 6 h.

Determination of wall-adsorbed residues: the bottle was rinsed three times with 30 ml acetone each, the combined solvent evaporated to dryness on a rotary evaporator, the residue dissolved in 5 ml methanol and diluted with water to 10 ml.

3. Results and discussion

3.1. Method development

3.1.1. HPLC separation

The pK_a values in Table 1 indicate a wide range from medium-strength acids (dicamba) to weak bases (prochloraz). Water solubilities vary over seven decades. A reversed-phase (RP) C_{18} HPLC column with spherical particles using a pH–acetonitrile gradient elution and diode array UV detection provides the selectivity and resolution required for that great span of properties. An NH_4Ac buffer system was utilised for pH gradient elution, already with view to facilitate a future combination with mass spectrometry (MS). Preliminary experiments showed that at pH 4 dicamba was sufficiently retarded from the solvent peak to allow peak area measurement although it is nearly fully deprotonated at this pH. This is attributed to the acetate effect [17]: HAc in the mobile phase causes organic acids to be retarded stronger than expected by hydrophobic stationary phases even at those pH values, at which they are already anionic. Prochloraz on the other hand is 30–40% protonated at pH 4 and therefore moves rather fast. The pH gradient was raised from 4 to 6 in order to suppress protonation of prochloraz and elute it in a useful range. Only a methyl-deactivated C_{18} material was able to produce a satisfactory peak profile for prochloraz. A MeCN gradient was superimposed to elute hydrophobic compounds. The complete ternary gradient is shown in Table 2 and yields separation of all analytes (Fig. 1), except diastereoisomers of propiconazole and cypermethrin.

Both cypermethrin and deltamethrin have three chiral centres yielding four pairs of diastereoisomers. Sales products contain deltamethrin in one isomeric form only, cypermethrin, however, as a mixture of isomers. The working calibration solutions were prepared accordingly and the HPLC chromatogram contains one peak for deltamethrin and three for cypermethrin (two diastereoisomers are superimposed). Cypermethrin was quantified by summing up all three peaks although a certain error may arise if the isomeric ratio is not identical in sample and calibration runs. This error, however, is apparently small since the measurement of the sales product cymbigon revealed the specified content of active

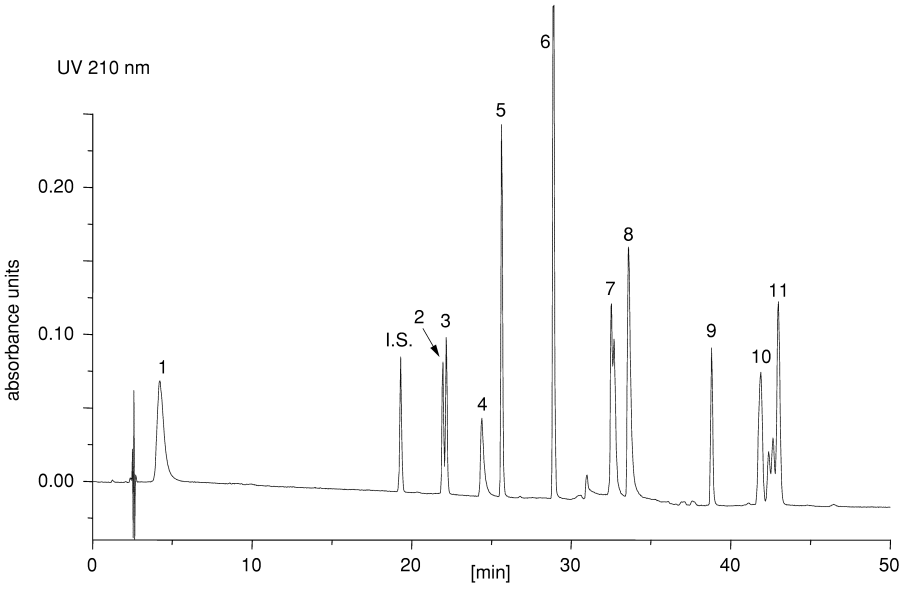

Fig. 1. Standard chromatogram from a composite calibration solution, mass concentration=10 μg ml^{-1}. Column and gradient – see text. Identification: dicamba (1), phenacetin (I.S.), thifensulfuron-methyl (2), methsulfuron-methyl (3), mecoprop (4), isoproturon (5), phenmedipham (6), propiconazol – two diastereomers (7), prochloraz (8), pendimethalin (9), cypermethrin – four diastereomers (10), deltamethrin (11).

ingredient. Propiconazole has two pairs of diastereoisomers and hence appeared as double peak which was also integrated in sum.

3.1.2. Basic calibration

The calibration plots established with peak areas were almost linear in the range from 1 to 50 μg ml^{-1} for each analyte with $r>0.99$. Intercepts were clearly smaller than the signal of the lowest calibration concentration. The relative procedural standard deviations based on the intermediate concentration of 25 μg ml^{-1} were between 0.5 and 4%. This proved, that linear calibration functions are valid for routine calibration.

All analytes revealed homogeneity of variances except the sulfonylureas and prochloraz. The reason for prochloraz is not clear, but for the sulfonylureas it is a stability problem of the calibration solutions. The sulfonylureas and phenmedipham turned out to be the most critical substances in this respect. Sulfonylureas are stable at pH 7, but are hydrolysed rather rapidly in acidic or basic media, phenmedipham on the other hand is hydrolysed at pH 7 but is very stable at pH 5. A compromise was a mixture of pH 6 buffer and methanol for the calibration solutions. The decomposition is reduced thereby to <5% in 3 days.

Short-term stabilities of relative response factors based on the internal standard were in a range of ±2.5% of the average. Therefore we adopted a two-point calibration with composite working calibration solutions set at 2 and 10 μg ml^{-1}, respectively, and an injection scheme as outlined in Section 2.7. However, not more than 10 samples should be run in duplicate within one measurement series. Then the calibration should be checked by control runs.

3.1.3. Extraction and sample work-up

The analytes were extracted from the Tenax sorbent medium by a simple batch extraction using the smallest volume of a water-miscible solvent, methanol. An aliquot was diluted with water before injection to decrease the eluting strength. We compared the extracting properties of methanol and acetonitrile and found, that, although acetonitrile removed the analytes better from Tenax, its eluting strength required a 1:2 dilution with water instead 1:1 for methanol, which was selected after all as the best compromise between recoveries, dilution factor and chromatographic performance. Injection volumes up to 10 μl were tolerated.

With batch elution the sampling and backup layers can be extracted and processed separately. Experiments with generated test atmospheres showed, that the extraction of the sampling layer only is necessary under normal sampling conditions, but it is very important to add both, the front and intermediate glass wool plugs, to the sorbent to be extracted. Extended ultrasonication has to be avoided since the Tenax material disintegrated easily causing problems with filtration.

The time needed for one sample from expelling the sorbent material until the final solution for HPLC injection was about 20 min.

3.1.4. Air sampling

The principles and experimental conditions of personal active air sampling of plant protectants using solid sorbent collecting tubes are documented in the literature [2,14,15]. According to their highly variable vapour pressures between 10^{-3} and 10^{-10} Pa (Table 1) they belong to the semivolatile organic compounds (SVOCs) [18] which occur simultaneously as vapours, as aerosols or bound to airborne particles. Little is known about the actual phase distribution in the atmosphere, however it is only necessary to strive for a simultaneous collection and extraction of vaporous as well as all inhalable particulate analytes.

This is accomplished by an experimentally simple sampling convention: the linear air flow velocity at the entrance opening of the sampling tube must be adjusted to 1.25 m s^{-1} ±10%. However, discussion is still in progress if sampling following this convention is indeed able to collect that fraction of particle sizes, which is defined as the inhalable fraction in the EN 481 [19,20], with sufficient accuracy. In the meantime this sampling convention is still accepted [14].

3.2. Method performance

3.2.1. Recoveries and method detection limits

The limits of quantification, the recoveries in the lower working range and their precisions were

Table 3
Recovery data and method detection limits (MDLs) from sorbent media fortified with pure active ingredients

	Fortification level (μg)	Mean recovery±SD (n=7) (%)	MDL (μg m^{-3})
Dicamba	30	105±3	3.0
Mecoprop, MCPP	70	103±4	9.1
Thifensulfuron-methyl	30	98±2	2.0
Metsulfuron-methyl	30	99±2	2.6
Pendimethalin	20	92±3	2.3
Isoproturon	15	95±2	1.0
Phenmedipham	15	99±4	2.1
Propiconazole	55	94±4	9.1
Prochloraz	30	94±4	4.8
Cypermethrin	50	92±3	5.3
Deltamethrin	30	89±3	3.8

MDLs are determined according to Ref. [21] to give a measure for the limit of quantification.

determined from a series of sorbent tubes, all identically fortified as described in Section 2.8.1, and are given in Table 3. All sampling tubes were analysed independently from each other using the two-point routine calibration scheme (Section 2.7). The quantification limits were calculated as method detection limits (MDLs) following a concept, which was originally derived for water analysis [21].

These MDL data can be compared with concentrations calculated from ADI values as proposed by Placha-Puller et al. [16], which can be regarded as criteria for the minimum concentrations that should be measurable with this method. For most compounds the actual MDLs were lower, for prochloraz and deltamethrin somewhat higher, only for mecoprop this minimum concentration is 1.0 μg m^{-3}. However, these calculated concentrations are not references in the strict sense since ADI values from different sources are highly variable (see Table 1) and some are denoted as preliminary ones. As a whole the method is sufficiently sensitive for monitoring purposes.

Possible breakthrough was tested by blowing air under sampling conditions through collecting tubes fortified with analytes: for 8 h at 2 l min^{-1} and at two different climatic conditions, 23°C/30% relative humidity and 35°C/80% relative humidity. No breakthrough was observed, all recoveries obtained from the sampling layer were around 100%.

Finally the sorbent material was fortified at two concentrations with solutions of some best-selling sales products containing the analytes, and air blown-through for 1 h. The mean recoveries obtained for the active compounds in these products were between 100 and 125%. However, the only reference was the content specified on the label or in the users instruction sheet. The formulation ingredients did not interfere in any case investigated, a typical chromatogram is shown in Fig. 2.

3.2.2. Recoveries from a generated test atmosphere

It is well known, that recovery experiments with the analytes applied directly into the sorbent medium never reflect the real processes during air sampling carried out while field spraying is in progress, in particular the vapour/particle phase distribution is neglected.

A model design to simulate the field conditions in the laboratory is published in the literature [14]: a test atmosphere was produced by spraying standard solutions of the active compounds into a spray-chamber under well defined conditions. The authors determined the aerodynamic diameters of the generated particles by physical methods and found 90% of them being between 0.1 and 2 μm. Sampling was performed by drawing air out of this test atmosphere with the same equipment and volumetric flow as used in routine sampling.

We adopted this approach, assuming that the same particle size distribution is produced if the experimental design and operation is repeated, in particular if the same spray-nozzle is utilised. Pendimethalin, isoproturon and metsulfuron were selected since their vapour pressures vary over seven

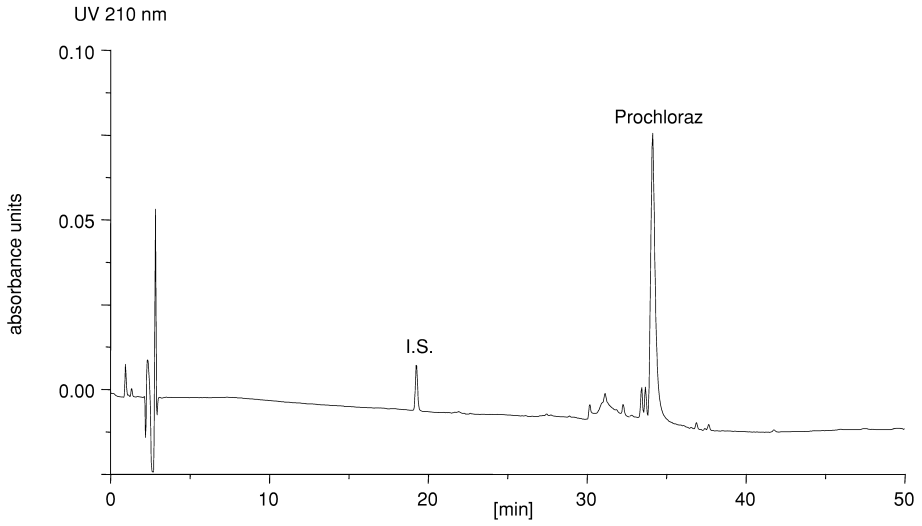

Fig. 2. Chromatogram obtained from a processed Tenax sampling tube fortified with sportak. The fortified amount is equivalent to 200 μg pure a.i. Conditions as in Fig. 1.

decades. The concentrations were then measured using the method under study and compared with the introduced ones – for results see Table 4. Expected concentrations inside the spray chamber were calculated from the masses introduced minus the amounts deposited on the inner wall and the air volume flowing through the chamber. The degree of wall-adsorption is higher for less volatile compounds, although it is distinctly lower than mentioned in literature [14] for compounds with similar vapour pressures. The reason for this might be, that the wall temperatures were about 10°C higher than the air temperature inside the chamber.

Sample and backup layers were analysed separately to detect possible breakthrough: it was not significant in these experiments. The recovery data in Table 4 were derived from processing the sample layer only. Although the recoveries are acceptable these results should be taken as an indication only, that the analytical method works properly, because the quantities charged are rather high. However, it was not recognised at this time, that the field

Table 4
Comparison of calculated and measured concentrations of a.i. in a generated test atmosphere

	Amount introduced (μg)	Wall adsorbed (μg)	Calculated concentration in air (μg m^{-3})	Collected amount		Measured concentration in air (μg m^{-3})	Recovery (%)
				Sampling layer (μg)	Backup layer (μg)		
Pendimethalin	1420	10	240	150	0	210	90
	1000	10	170	100	0	140	80
	680	10	110	60	0	80	70
Isoproturon	1730	160	260	140	20	190	70
	1210	110	180	100	10	140	80
	880	100	130	70	10	100	80
Metsulfuron	2780	290	420	310	10	430	100
	1940	180	290	190	10	260	90
	1390	150	210	150	10	210	100

Figures are rounded to the nearest 10 μg, mg m^{-3} or %.

measurements would render quite lower concentrations.

3.2.3. Field evaluation

Field measurements were performed as means to assess the general utility of the method. Special attention was given to possible interferences from organic air constituents that may be present in a farmstead. The air pump worn by the farmer was not turned off when he moved to other activities between spraying work.

Field sprayers equipped with horizontal spray booms at 50 cm height and nozzles directed downwards were used for all test runs in Table 5, except run 5, where the height was 1.5 m. Driver cabins were open to the rear only. Wind was gentle and rather constant. Therefore the low concentrations found are not surprising, a significant exposure might be a result of adverse wind conditions that directs the sprayed chemicals into the driver cabin. The value for thifensulfuron-methyl appears somewhat high, especially if compared with the amount dispersed. This could have been collected during mixing or filling of the spray-broth or cleaning of the equipment, because the sampling pump was turned on during these operations also.

4. Conclusion

The practicability of a multiclass/multiresidue method was demonstrated for measurement of some prevalent plant protecting agents in air with personal active sampling. The method involves four unit operations only: sampling – elution – dilution – HPLC measurement. The ''acetate-effect'' and a pH elution gradient enables the HPLC separation of all compounds in one single chromatographic run. Method performance was tested with a reference atmosphere generated in a spray chamber and containing both, vaporous as well as particulate analytes, and finally with some field spraying trials.

Forthcoming work will proceed in three directions: (1) investigation of some new HPLC stationary phases, especially those with hydrophilic endcapping, which promise better peak performance and therefore a more rapid elution, (2) exploring the potential of microbore HPLC when incorporated into

Table 5
Results of field evaluation

Application				Measurement	
Product	a.i.	Total amount (g)	Area (ha)	Concentration ($\mu g\ m^{-3}$)	Amount inhaled (μg)
Alon Starane 250 Dicopur Urea	Isoproturon Fluroxypyr 2,4-D	7500	10	3.5	25
Concert	Thifensulfuron-methyl Metsulfuron-methyl	470 47	8	n.d. n.d.	
Concert	Thifensulfuron-methyl Metsulfuron-methyl	118 12	2	2.9 n.d.	15
Alon	Isoproturon	2500	2	n.d.	
Decis	Deltamethrin	31	5	n.d.	
Stomp	Pendimethalin	5600	4	d.	
Sportak 45 EC Alto 100 SL	Prochloraz Cyproconazol	2250	7	d.	

n.d.: Not detected; d.: detected, but below MDL.

this method and (3) the extension of the method to fruit and wine growing preparations and also those applied in regions with subtropical or even tropical climatic conditions.

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