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Sensitive, simultaneous determination of P, S, Cl, Br and I containing pesticides in environmental samples by GC hyphenated with collision-cell ICP-MS

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A sensitive and highly selective methodology for the determination of a wide range of pesticides, based on the simultaneous element-specific determination of phosphorus, sulfur, chloride, bromine and iodine by gas chromatography hyphenated with octopole reaction cell-inductively coupled plasma mass spectrometry (GC-CC-ICP-MS) is described. The chromatographic system was optimised for separation efficiency and short run times and was coupled *via* a commercially available interface with an octopole reaction cell ICP-MS system which is equipped with an on-axis collision cell. Instrumental settings were optimised with respect to high sensitivity for the target nuclides ^{31}P, ^{32}S, ^{35}Cl, ^{79}Br and ^{127}I and minimized background levels especially for the ions most affected by interferences, such as $^{31}P^+$, $^{32}S^+$. Helium and nitrogen were tested as additional plasma gases for possible sensitivity enhancement of the element-specific detection resulting from improved ionisation processes inside the plasma. Due to the multi-element capability of the instrumental setup and the good accuracy of the retention times that were achieved, identification of the detected pesticides can be carried out using their retention times, the element compositions and element ratios present in each chromatographic peak. For the different pesticides detection limits down to the ppt level or the low ppb level were obtained. The average RSDs of the retention times and the peak areas were better than 0.8% and 8%, respectively. The analytical methodology developed has been applied to the screening of different fruit extracts for pesticides. Peaks were identified by comparison of the retention times obtained and by their elemental composition. Quantitative results have been obtained both by external calibration and by using a compound independent calibration.

Introduction

The extensive and still growing use of pesticides in agriculture and forestry represents the main source for the widespread distribution of these compounds and their degradation products in the environment.[1] Due to their persistence in the environment and their lipophilic character, which causes bioaccumulation and therefore their presence in the food chain, the use of different organochlorine pesticides has been restricted or banned for several years. Nevertheless, they are being used illegally in many countries. Organophosphorus and carbamate-based pesticides have now superseded the organochlorine pesticides, but their residues and degradation products can also be found in the environment and in the food chain. Since the ratification of the EU water framework directive in 2000, which was developed for an integrative protection of EU drinking water resources, various pesticides, such as Chlorpyrofos ($C_9H_{11}Cl_3NO_3PS$), Chlorfenvinphos ($C_{12}H_{14}Cl_3O_4P$) or trichlorobenzenes ($C_6H_3Cl_3$), have also been listed as priority substances which affect the chemical water quality.[2] Regulation and monitoring of the substances listed and the actual state of the water or food quality requires analytical techniques which allow sensitive and fast screening for a wide range of compounds.

Gas chromatography (GC) and high-performance liquid chromatography (HPLC) in combination with different detection methods represent the preferred techniques for the determination of pesticides.

Since almost all pesticides contain heteroatoms, element selective detectors such as nitrogen–phosphorous (NPD),[3,4] flame photometric (FPD)[5,6] and electron capture detectors (ECD)[7,8] have commonly been used in combination with GC separations.

In recent years mass spectrometry (MS) or tandem mass spectrometry (MS/MS) employing different ionisation sources have been used for the sensitive and molecule-selective determination of pesticides and their degradation products, either in combination with GC or HPLC.[8–11]

Atomic emission detection (AED) provides highly element-specific detection of the hetero-elements nitrogen, chlorine, phosphorus, sulfur, bromine and fluorine, which are important elements in pesticide residue analysis.[12–14] The main drawback of AED is its overall low sensitivity.[15]

The hyphenation of GC and inductively-coupled plasma mass spectrometry (ICP-MS) represents an alternative approach to the sensitive and simultaneous element-specific determination of hetero-elements such as phosphorus, sulfur, chlorine, bromine and iodine in pesticides. The determination of these elements by ICP-MS is still a challenging task: all the elements mentioned show high first ionisation potentials and low ionisation efficiency in an argon based plasma. Due to the formation of molecular ions such as $^{14}N^{16}O^1H^+$ or $^{16}O_2^+$ inside the argon plasma, the detection of phosphorus and sulfur is significantly disturbed. Table 1 gives an overview of the ionisation characteristics of the relevant elements.[16]

Therefore, a sensitive determination of phosphorus and sulfur after GC separation has mainly been achieved with high resolution ICP-MS (HR-ICP-MS). Rodriguez-Fernandez *et al.* have used GC-HR-ICP-MS for the speciation of sulfur containing compounds in human breath.[17]

The special plasma conditions that can be achieved when using GC for sample introduction, namely a dry plasma and

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Table 1 Overview of the ionisation potential, ionisation efficiency and the main interfering ions of the heteroelements investigated (taken from ref. 16)

Element	Isotopes	1st ionisation potential/eV	Ionisation efficiency in an argon plasma	Main interfering ions
P	^{31}P	10.484	35	$^{14}N^{16}O^{1}H^{+}$
S	^{32}S, ^{33}S, ^{34}S, ^{36}S	10.357	15	$^{16}O_2^{+}$
Cl	^{35}Cl, ^{37}Cl	13.01	<1	
Br	^{79}Br, ^{81}Br	11.84	5	
I	^{127}I	10.454	30	

almost no matrix which can cause the formation of interfering molecular ions, also offer the possibility of using quadrupole based ICP-MS (ICP-QMS) for element-specific detection of hetero-element containing substances.

Pavageau has used GC-ICP-QMS for the determination of phosphine emissions in a tobacco factory based on ^{31}P detection.[18] Meija *et al.* have used ICP-QMS hyphenated with GC for the determination of volatile sulfur and selenium species emitted by *Brassica juncea* using ^{34}S.[19] Recent papers have also described the use of GC-ICP-QMS for the determination of chlorine,[20] bromine,[21,22] and iodine[22–24] containing compounds. Recently Bouyssiere *et al.* have given a general overview of the fields of application of GC-ICP-MS.[25]

Since the introduction of collision/reaction cell technology onto the market, quadrupole based ICP-MS (CC-ICP-MS) systems have also been used for the sensitive determination of phosphorus and sulfur together with high-performance liquid chromatography (HPLC)[26–28] or capillary electrophoresis (CE)[26,29,30] for sample introduction, which implicates an increased matrix intake (*e.g.*, water, solvents, buffer-salts) into the plasma. Collision-cell technology enables the sensitive determination of elements normally affected by interferences such as phosphorus or sulfur, based on the chemical or physical resolution of the elements of interest from the interfering polyatomic ions generated in the argon ICP due to the application of reactive gases or kinetic energy discrimination. A recent paper describes the application of GC-CC-ICP-MS for the detection of pesticides due to their phosphorus content.[31]

The combination of GC as sample introduction technique, which generates a dry and nearly matrix free plasma, and a sensitivity improved collision-cell ICP-MS system capable of further reducing interfering polyatomic ions is a promising new analytical approach for a variety of new applications based on the element-specific determination of more or less volatile, hetero-element containing substances such as pesticides, flame retardants or petroleum products.

The present paper describes the use and optimisation of GC hyphenated with an Agilent 7500cs collision cell ICP-MS for the sensitive simultaneous element-specific determination of phosphorus, sulfur, chlorine, bromine and iodine containing pesticides in one single chromatographic run and its application to pesticide screening in fruit and vegetable samples.

Experimental

Chemicals and standards

Ultra pure water (18 MΩ cm) was prepared using a Millipore Elix 3/Milli-Q Element water purification system (Millipore, Milford, MA, USA).

Nitric acid (65%, Suprapur) was obtained from Merck (Merck, Darmstadt, Germany) and further purified by sub-boiling distillation in a quartz apparatus (Kürner, Rosenheim, Germany).

n-Hexane (p.a., Merck) was used as solvent and for sample dilution.

Helium 5.0 (99.999%) was used as GC carrier gas, as the collision gas inside the octopole reaction system and as the additional plasma gas for sensitivity enhancement. Nitrogen 5.0 (99.999%) was also used as an additional plasma gas. A mixture of 20% sulfur hexafluoride 3.0 (99.9%) in helium 5.0 (99.999%) (v/v) was used for the sulfur specific tuning of the ICP-MS. Xenon 4.8 (99.998%) was used for general tuning of the GC-ICP-MS setup. Argon 5.0 (99.999%) was used as plasma gas and carrier gas for the GC interface. All gases were obtained from Messer Griesheim (Messer Griesheim, Krefeld, Germany).

Single compound pesticide standards (Chlorpyrifos-methyl ($C_7H_7Cl_3O_3PS$), Prothiofos ($C_{11}H_{15}Cl_2O_2PS_2$), Phorate ($C_7H_{17}O_2PS_3$), Disulfoton ($C_8H_{19}O_2PS_3$), Fenthion ($C_{10}H_{15}O_3PS_2$), Fensulfothion ($C_{11}H_{17}O_4PS_2$), Sulprofos ($C_{12}H_{19}O_2PS_3$) and Azinphos-methyl ($C_{10}H_{12}N_3O_3PS_2$)) were obtained from Fluka/Riedel de Haën (Pestanal, Fluka/Riedel de Haën, Taufkirchen, Germany).

Pesticide mixtures containing Phorate, Chlorphyrifos ($C_9H_{11}Cl_3NO_3PS$), Diazinon ($C_{12}H_{21}N_2O_3PS$), Pentachloronitrobenzene ($C_6Cl_5NO_2$), Dichlobenil ($C_7H_3Cl_2N$), 1,2,3-trichlorobenzene ($C_6H_3Cl_3$), 4,4′-dibromooctafluorobiphenyl ($C_{12}Br_2F_8$), 2,4,6-tribromoanisole ($C_7H_5OBr_3$), Terbufos ($C_9H_{21}O_2PS_3$), Malathion ($C_{10}H_{19}O_6PS_2$), Ethoprofos ($C_8H_{19}O_2PS_2$), Silvex methyl ester/Fenoprop ($C_9H_7Cl_3O_3$), decachlorobiphenyl ($C_{12}Cl_{10}$), Ioxynil-methyl ($C_8H_5NOI_2$)and triphenyl phosphate ($C_{18}H_{15}O_4P$) (CUS-3217) or Fensulfothion, Azinphos-methyl, Coumaphos ($C_{14}H_{16}ClO_5PS$), Demeton ($C_8H_{19}O_3PS_2$), Phorate, Disulfoton, Trichloronate ($C_{10}H_{12}Cl_3O_2PS$), Fenthion, Tokuthion ($C_{11}H_{15}Cl_2O_2PS_2$) and Bolstar/Sulprofos) ($C_{12}H_{19}O_2PS_3$) (SPM-622A) with different concentrations were obtained from Ultra Scientific (Ultra Scientific Europe, Wesel, Germany).

GC

An Agilent 6890 gas chromatography system (Agilent Technologies, Waldbronn, Germany) equipped with an Agilent 7683 series autosampler and a split/splitless injection port was used in this work. The GC was also equipped with an additional 3 way gas-flow controller which allows the precise mixing of different gases to the ICP-MS controlled carrier-gas. Details of the chromatographic conditions are given in Table 2.

Table 2 Instrumental parameters of the GC-ICP-MS setup used

GC parameters—	
Column	Agilent HP5MS, 30 m , id 0.25 mm, film thickness 0.25 μm, 5% phenyl, 95% methyl polysiloxane
Carrier gas	Helium
Carrier gas flow rate	2 ml min^{-1}
Injection volume/mode	1–5 μL, pulsed splitless, 60 psi, 0.5 min
Injector temperature	250 °C
Temperature program	Initial temperature 70 °C hold for 1 min, ramp of 30 °C min^{-1} to 300 °C hold for 5 min
GC-ICP-MS interface parameters—	
Transfer line/injector temperature	280 °C
ICP-MS parameters—	
Rf power	550 W
Carrier gas flow rate	0.9 L min^{-1}
Sampling depth	4.9 mm
Cones	Platinum
Cell gas flow rate	2.5 ml min^{-1} helium
Extraction lens	−180 V
Octopole bias	−14 V
Quadrupole bias	−2 V
Measured isotopes/ dwell time	^{31}P (0.2 s), ^{32}S (0.01 s), ^{34}S (0.2 s), ^{35}Cl (0.01 s), ^{79}Br (0.01), ^{127}I (0.01 s)
Optional plasma gas	He at 30 ml min^{-1} controlled by the GC

GC interface

A second generation Agilent GC-ICP-MS interface which features a temperature controlled silcosteel transfer-line and a new stainless steel injector tip was used for the hyphenation of GC and ICP-MS (Agilent Technologies, Tokyo, Japan). Details on the interface can be found elsewhere.[19] Detailed interface settings are summarized in Table 2.

ICP-MS

An Agilent 7500cs ICP-MS system (Agilent Technologies, Tokyo, Japan), which features an on-axis octopole ion guide that operates in an rf-only mode, a modified ion lens system and shield torch technology, was used as element-specific detector.

The ions were extracted by an omega lens-system, consisting of a dual extraction lens and an omega lens assembly for increased sensitivity, and with an off-axis design which provides an overall low background. The off-axis design prevents photons and neutral compounds from entering the on-axis reaction cell chamber. In contrast to the normal 7500c, the octopole is not tilted in accordance with the deflected ion beam. This configuration leads to a improved sensitivity.

Constant energy discrimination is implemented in order to attenuate low energy ions produced in the cell, as described elsewhere.[32,33]

In this study, the dc bias of the quadrupole was set at a less negative value compared with the setting of the octopole. When the collision cell is pressurised, the octopole bias is set at -14 V and the quadrupole bias is typically -2 V to -1 V. This was found to be optimal for elemental sensitivity and low background. Only helium was used as a cell gas with an optimum flow-rate of 2.5 mL min^{-1}.

Details concerning the ICP-MS settings are given in Table 2.

Sample preparation

Standard solutions. All daily working standards were obtained by dilution of gravimetrically prepared stock solutions of the investigated pesticides with hexane. All solutions were stored in glass vials which were cleaned with acid (1 mol L^{-1} HNO_3) and flushed with Milli Q. Prior to use all vials were flushed with hexane.

Fruit extracts. Fruit extracts were prepared by the California Department of Food and Agriculture (CDFA) and were provided by Agilent Technologies. They were prepared according to the procedure described by Cook *et al.*[34]

In brief, 50 g of homogenized fruits or vegetables were mixed with 100 mL of acetonitrile and shaken. The filtered extract was further purified by C-18 SPE and collected together with NaCl. After shaking and centrifugation, the residual water layer was drained off. The extract was evaporated in a steam bath to around 2 mL and finally air-dried. The dry extract was mixed with 2 mL of acetone and frozen to precipitate the NaCl. After thawing, the supernatant was used for pesticide residue analysis.

Results and discussion

Optimisation and characterisation of the cell settings

Due to the dry plasma conditions and the absence of nearly any interfering matrix when using GC for sample introduction, the measured background for all elements detected is quite low compared with wet plasma conditions. To further reduce the background, especially for ^{31}P and ^{32}S, cell gases such as He and Xe were tested. The best results were obtained with the addition of 2.5 mL min^{-1} He into the octopole reaction system (ORS). Fig. 1 shows the effect of the addition of helium to the

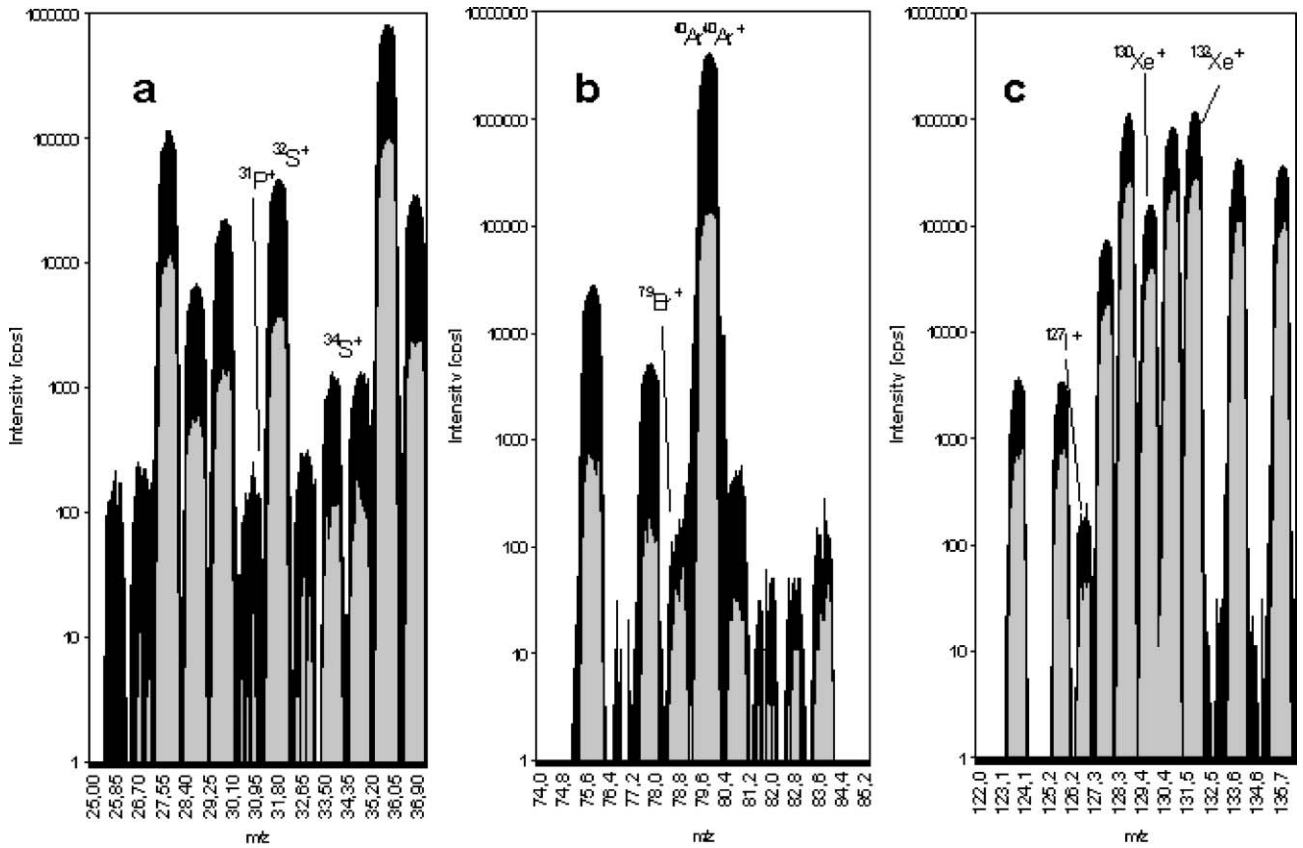

Fig. 1 Spectral background with and without the addition of 2.5 mL min^{-1} helium to the ORS. a, *m/z* 25–37; b, *m/z* 74–85; c, *m/z* 122–136. Black spectrum: no helium addition. Grey spectrum: addition of 2.5 mL min^{-1} to the ORS.

ORS on the spectral background. As can also be seen, ^{79}Br shows a better separation from the high abundance $^{40}Ar^{40}Ar^{+}$ dimer due to the addition of He to the collision cell.

$^{14}N^{16}O^{1}H^{+}$, $^{15}N^{16}O^{+}$ and $^{16}O_2{}^{+}$ are the most abundant polyatomic ions which interfere with the determination of phosphorus and sulfur using quadrupole-based ICP-MS. For the dissociation of $^{15}N^{16}O^{+}$ or $^{16}O_2{}^{+}$, collisional energies of 6.5 eV and 6.66 eV, respectively, are necessary.[35,36]

The collision energy obtained under the optimised instrumental settings realised, can be calculated according to

$$E_{cm} = \frac{m_k}{m_k + m_p} E_{lab} \quad (1)$$

where E_{cm} represents the collision energy at the centre of the mass, m_k the mass of the cell gas (He, 4.0026 u), m_p the mass of the target ion ($^{15}N^{16}O^{+}$, 30.99502 u, $^{16}O_2{}^{+}$, 31.9988 u) and E_{lab} represents the kinetic energy resulting from the potential difference between the extraction lens and the quadrupole entrance. With E_{lab} = 16 eV and He as cell gas, collision energies of about 1.8298 eV for $^{15}N^{16}O^{+}$ and 1.7788 eV for $^{16}O_2{}^{+}$ are obtained, which is not sufficient for the dissociation of the interfering ions inside the cell. Therefore, kinetic energy discrimination obtained by the settings of the octopole and quadrupole bias prevents interfering ions from entering the quadrupole mass filter. The interfering polyatomic ions were decelerated due to collisions with the helium gas used for pressurising the octopole reaction cell. Due to their larger cross section they collide more often with the He gas in comparison with the elemental ions under investigation. Finally, the huge energy barrier created by the octopole and quadrupole bias settings prevents these low energy ions from entering the quadrupole mass filter. Details on the principles and mechanisms of kinetic energy discrimination have been reported in detail elsewhere.[33]

Optimisation of the GC-ICP-MS settings

Extraction lens 1 voltage settings. The ICP-MS used can be operated with different extraction modes, namely soft extraction (positive extraction lens 1 voltage up to +10 V) or hard extraction (highly negative extraction lens 1 voltage down to −200 V).

By comparison with the Agilent 7500c ICP-MS system, which only shows minor differences between the hard and the soft extraction mode and therefore normally operates in the soft extraction mode due to the lower background level, the 7500cs system used shows a great dependency between its sensitivity and the extraction mode when hyphenated to GC.

Fig. 2 shows the effect of different extraction lens 1 voltage settings on the elemental response of some selected pesticides. The best sensitivity for all measured elements (P, S, Cl, Br, I) was obtained under hard extraction conditions (−180 V), which result in an acceleration of the ions behind the skimmer and therefore a more efficient extraction from the plasma. A minimum response was found between −20 V and 0 V. Higher positive voltages (between 0 and +10 V) result in an increasing elemental response which is approximately 5 times worse compared with the hard extraction settings (−180 V) used.

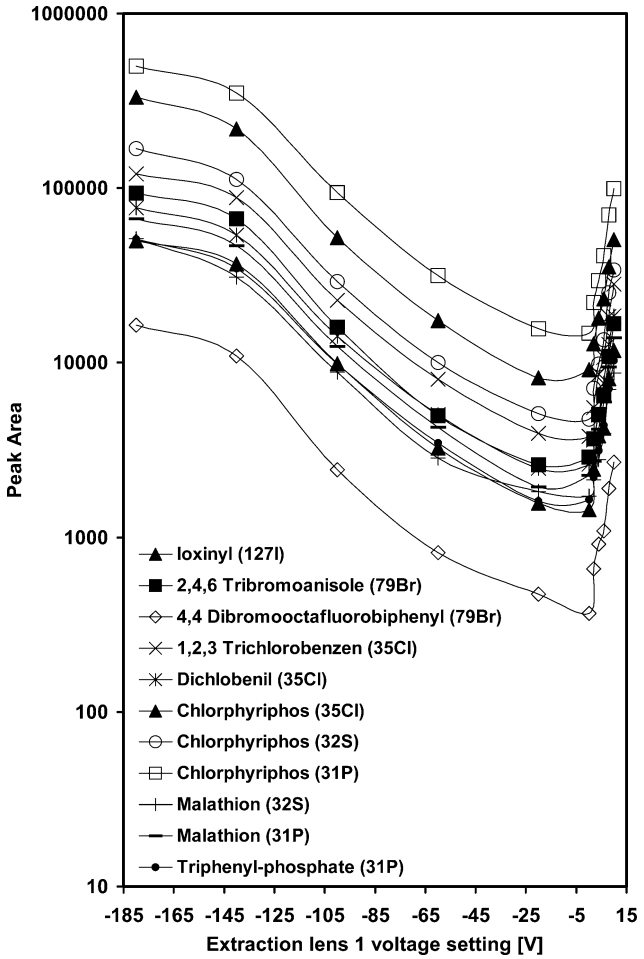

Fig. 2 Effect of the extraction lens 1 voltage settings on the elemental response of selected pesticides under GC-ICP-MS conditions. Injection of 1 μL CUS 3217 multicompound pesticide mixture.

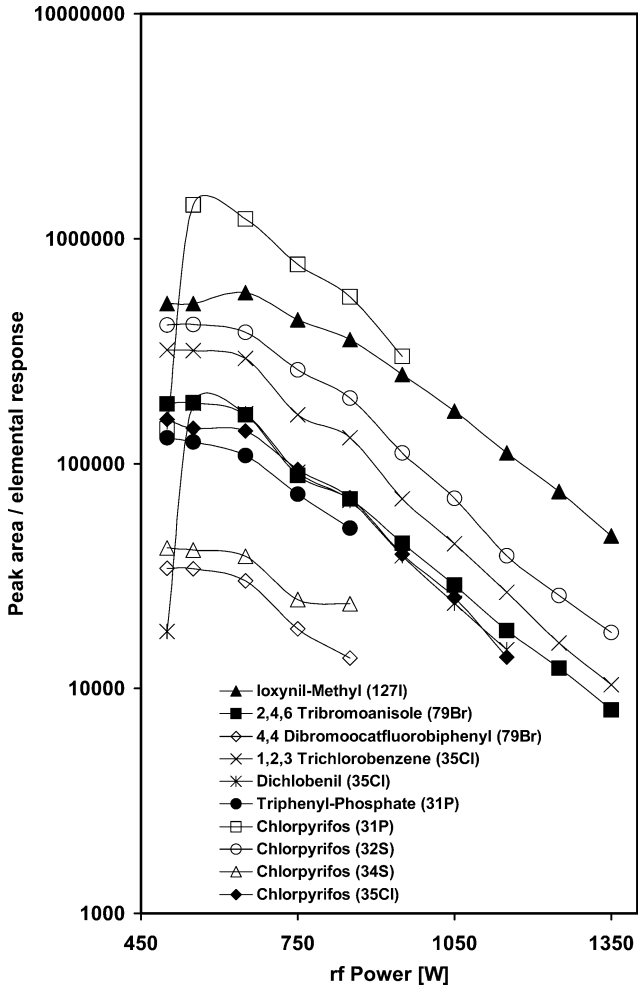

Fig. 3 Effect of the rf settings on the elemental response of selected pesticides under GC-ICP-MS conditions. Injection of 1 μL CUS 3217 multicompound pesticide mixture.

Therefore the hard extraction mode was used for all further experiments.

Rf power. Fig. 3 shows the optimisation of the rf power settings. A standard pesticide mixture (CUS 3217, 1000 times diluted, 1 μL pulsed splitless injection) was injected several times under different rf power settings.

The best sensitivity and signal to noise ratios for all isotopes evaluated were obtained under low rf power conditions due to the dry plasma conditions. Based on these results all further experiments were carried out under low plasma rf power conditions of 550 W.

Additional plasma gases. As described in the literature, the addition of carbon containing compounds (*e.g.* methanol)[37,38] or gases (*e.g.*, nitrogen, helium)[39,40] to the ICP can lead to an improved ionisation process for difficult to ionize elements such as P, S, Cl, Br or I.

Nitrogen and helium were tested as additional plasma gases for further signal enhancement due to improved ionisation of the target ions inside the plasma. The addition of these gases increased the overall sensitivity of the setup. Nitrogen, unfortunately, also caused an increased background on the mass of phosphorus due to the formation of $^{15}N^{16}O^{+}$ and $^{14}N^{16}OH^{+}$ ions.

Fig. 4a shows the effect of the addition of helium to the plasma on the signal intensities of some selected pesticides. The best signal to noise ratios were obtained by the addition of around 30 ml min^{-1} He (corresponding to a setting of 40 psi at the additional 3 way gas controller) to the argon carrier gas.

Fig. 4b shows the effect of the addition of nitrogen to the plasma for the same pesticides as before. Nitrogen also increased the sensitivity of the setup but excessive addition of nitrogen results in a drastically reduced overall sensitivity. Therefore, helium was added continuously to the plasma during all measurements.

Carrier gas flow rate. The carrier gas flow rate also has some impact on the analytical characteristics of the instrumental setup. Low carrier gas flow rates can improve the detection limits due to a reduced sample dilution and reduce the overall background due to a reduced matrix intake into the plasma (*e.g.*, GC capillary burn-off, matrix compounds of the carrier gas). The main problem of a low carrier gas flow rate is that it results in increased peak broadening. To avoid these problems, a medium carrier gas flow rate of 0.8 L min^{-1} was used during all experiments.

Figures of merit

Reproducibility. The reproducibility (peak areas and retention times) were calculated based on the data obtained by repetitive injections of a multi-compound pesticide mixture (Ultra Scientific, CUS 3217). Table 3 shows the reproducibility of the retention times and peak areas. RSDs better than 0.8% (retention time) and 8% (peak areas) were obtained indicating the good accuracy of the setup. This is a prerequisite for the retention time-based identification and multicompound screening of pesticides.

Detection limits. Table 4 shows the calibration curves obtained for the constituents of an SPM 3217 pesticide mixture. As can be seen from the mean and the RSDs of the

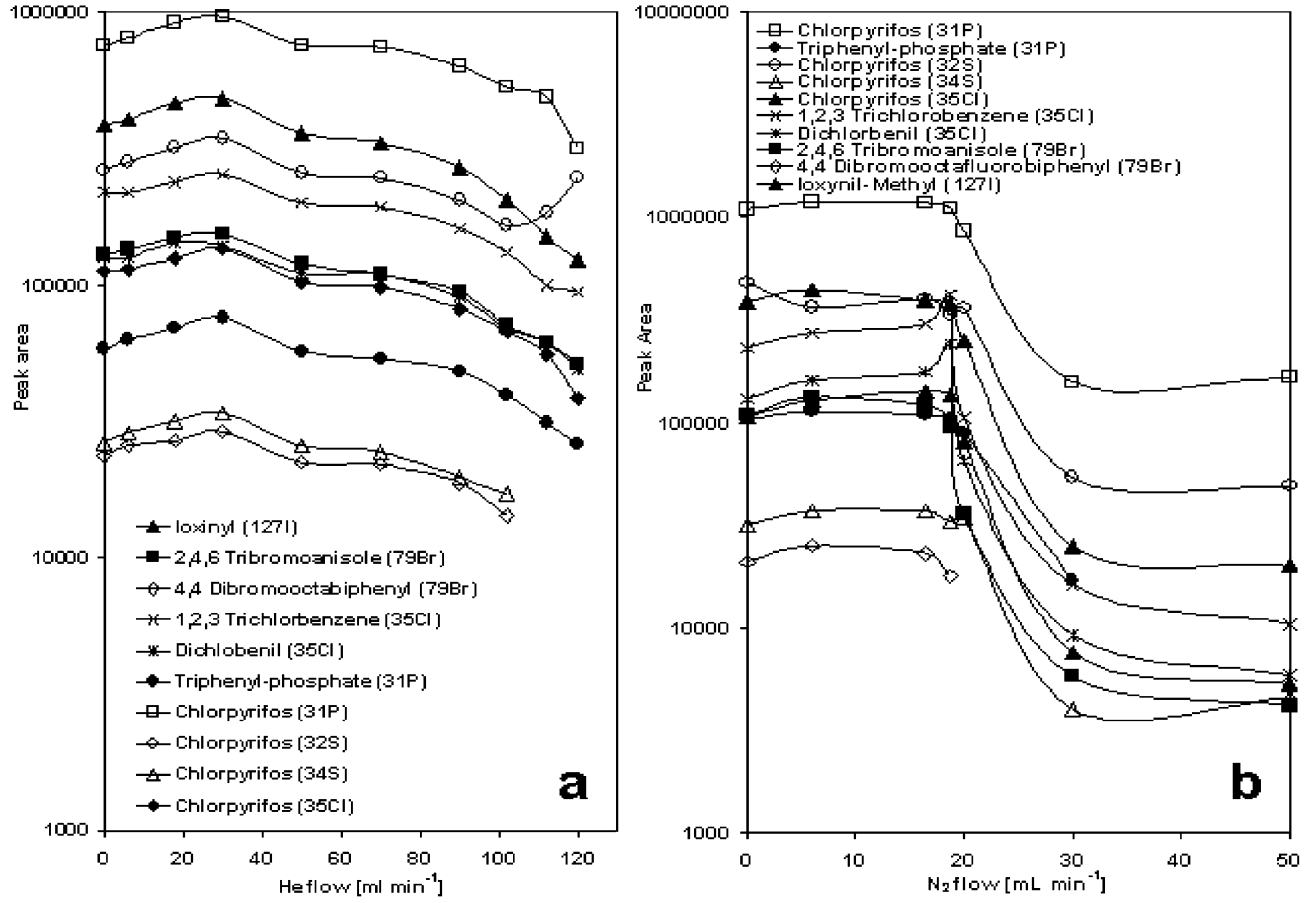

Fig. 4 Optimisation of the optional plasma gas flow: a, helium; b, nitrogen. Effect on the elemental response of selected pesticides. Injection of 1 μL CUS 3217 multicompound pesticide mixture.

Table 3 Peak area and retention time RSD (%) calculated after repetitive injections of CUS-3217 pesticide mixture ($n = 7$, 1/100 000 diluted in n-hexane, 5 μL injection)

Compound	Element	Peak area RSD (%)	Retention time RSD (%)
1,2,3-Trichlorobenzene	^{35}Cl	2.03	0.34
Dichlobenil	^{35}Cl	4.65	0.04
2,4,6-TBA	^{79}Br	1.73	0.22
Ethoprop	^{31}P	2.65	0.03
4,4-DBOP	^{79}Br	3.30	0.22
Phorate	^{31}P	1.81	0.04
Pentachloronitrobenzene	^{35}Cl	3.46	0.03
Tebufos/Diazinon	^{31}P	4.48	0.08
Ioxynil-Methyl	^{127}I	5.31	0.01
Malathion	^{31}P	7.25	0.02
Chlorpyrifos	^{31}P	5.90	0.03
Triphenylphosphate	^{31}P	4.33	0.72

calibration curve slopes the elemental response of the setup is independent of the species used for obtaining the calibration curve. This is a prerequisite for a compound independent calibration (CIC).

Table 5 summarizes the detection limits calculated according to the IUPAC guideline (3 times standard deviation of the background divided by the slope of the calibration curve) obtained for some selected pesticides present in the CUS 3217 pesticide mixture.

Depending on the element used for the calculation and the compound, detection limits down to the ppt level or the low ppb level, respectively, were derived. This is a promising result for the sensitive determination of pesticides in real world samples.

In comparison with other detection techniques used for routine pesticide determination (*e.g.*, GC/MS, GC/AED, GC/NPD) which often include preconcentration and enrichment steps such as solid-phase extraction (SPE) or solid-phase microextraction (SPME), up to two orders of magnitude better detection limits have been achieved with the proposed GC-CC-ICP-MS setup.

Fig. 5 presents the separation of a 1 : 1000 diluted SPM 3217 sample.

Fig. 6 shows the separation of a multi-compound pesticide mixture under optimised conditions. This also indicates the high separation efficiency and selectivity due to the element specific detection.

Table 5 Estimation of the detection limits (μg L^{-1}) according to the IUPAC guidelines (3 × s.d. of the background/slope of the calibration curve) (CUS-3217 pesticide mixture, 1 μL injection)

Compound	Element	Detection limit compound	Detection limit element
1,2,3-Trichlorobenzene	^{35}Cl	1.8	1
Dichlobenil	^{35}Cl	2.5	1
2,4,6-TBA	^{79}Br	0.3	0.2
Ethoprop	^{31}P, ^{32}S	0.2/4	0.02/1
4,4-DBOP	^{79}Br	0.5	0.2
Phorate	^{31}P, ^{32}S	0.2/3	0.02/1
Pentachloronitrobenzene	^{35}Cl	4	3
Tebufos	^{31}P, ^{32}S	0.2/3	0.02/1
Diazinon	^{31}P, ^{32}S	0.3/10	0.03/1
Ioxynil-Methyl	^{127}I	0.02	0.01
Malathion	^{31}P, ^{32}S	0.2/7	0.02/1
Chlorpyrifos	^{31}P, ^{32}S, ^{35}Cl	0.2/11/9	0.02/1/3
Triphenylphosphate	^{31}P	0.4	0.04

Application to real samples

Five different real samples extracted from fruits and vegetables were analysed under optimised instrumental conditions. Pesticides were separated and identified either by their retention times or their elemental composition. Currently, the retention times of 47 compounds have been verified with the separation settings used. Quantification was performed by external calibration provided that calibration data were available.

Fig. 7 shows the separation of a tomato extract by GC-CC-ICP-MS. The same sample was evaluated by GC-MS and about 31 μg L^{-1} of Chlorpyrifos was found.

Using GC-CC-ICP-MS, concentrations of 33.,79 μg L^{-1} (^{31}P), 31.39 μg L^{-1} (^{32}S) and 32.02 μg L^{-1} (^{35}Cl) were calculated by external calibration, depending on the element used. These results show a good agreement between GC-CC-ICP-MS and GC-MS.

The SPM 3217 standard mixture includes phosphorus, sulfur and chlorine containing pesticides with different concentrations which results in a wide range of elemental concentrations, depending on the compound. A single chromatographic separation therefore provides enough data for a compound independent calibration (CIC). 1 μL of a 1 : 1000 diluted SPM 3217 pesticide mixture sample was injected on the GC column. For ^{31}P, ^{32}S and ^{35}Cl the calibration curves can be expressed as:

Table 4 Calibration graph functions based on the elemental response of the GC-ICP-MS setup (equation $y = bx + a$, y = peak area, b = slope of the calibration curve, a = y axis intercept, x = concentration in μg L^{-1})

		^{31}P			^{32}S			^{35}Cl $^{(\#)}$, ^{79}Br $^{(*)}$ ^{127}I $^{(+)}$		
Compound	Retention time/min	b ($\times 10^3$)	a ($\times 10^3$)	R^2	b ($\times 10^3$)	A ($\times 10^3$)	R^2	b ($\times 10^3$)	a ($\times 10^3$)	R^2
1,2,3 Trichlorobenzene	7.51							$0.78^{(\#)}$	$-24.39^{(\#)}$	$0.9999^{(\#)}$
Dichlobenil	9.12							$0.78^{(\#)}$	$-16.86^{(\#)}$	$0.9999^{(\#)}$
2,4,6-Tribromoanisole	14.13							$0.95^{(*)}$	$-3.85^{(*)}$	$1^{(*)}$
Ethoprop	14.35	20.58	−3.56	0.9999	7.04	−57.89	0.9999			
4,4-Dibromooctabiphenyl	15.48							$0.95^{(*)}$	$-1.09^{(*)}$	$1^{(*)}$
Phorate	15.83	23.67	−15.85	1	7.92	−25.88	0.9999			
Pentachloronitrobenzene	17.62							$0.77^{(\#)}$	$-16.40^{(\#)}$	$0.9999^{(\#)}$
Terbufos	17.94	24.74	−75.33	0.9999	7.67	−42.75	1			
Diazinon	18.59	24.62	−73.89	0.9999	8.03	−18.79	1			
Ioxynil Methyl	21.08							$10.78^{(+)}$	$-5.44^{(+)}$	$1^{(+)}$
Malathion	23.13	19.21	−6.29	0.9999	6.35	−13.33	1			
Chlorpyriphos	23.59	23.83	−37.18	0.9999	7.83	−12.36	0.9999	$0.75^{(\#)}$	$-18.80^{(\#)}$	$1^{(\#)}$
Triphenylphosphate	30.30	22.16	−2.72	1						

	^{31}P	^{32}S	^{35}Cl	^{79}Br
Mean slope (b) ($\times 10^3$)	22.73	7.47	0.77	0.95
RSD (b) (%)	9.15	8.73	2.08	0.34

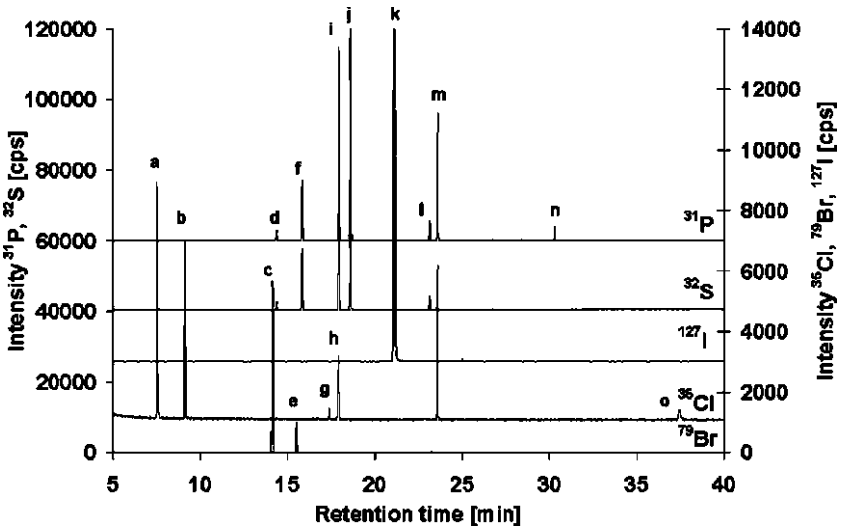

Fig. 5 Separation and heteroelement-specific detection of a multicompound pesticide mixture (CUS 3217, 1/1000 in n-hexane, 1 μL pulsed splitless injection) by GC-ORS-ICP-MS. Peak assignment and retention order: a, 1,2,3-trichlorobenzene; b, Dichlobenil; c, 4,4-dibromooctafluorobiphenyl; d, Ethoprop; e, 2,4,6-tribromoanisole; f, Phorate; g, Silvex; h, pentachloronitrobenzene; i, Terbufos; j, Diazinon; k, Ioxynil-Methyl; l, Malathion; m, Chlorphyrifos; n, Triphenylphosphate; o, Decachlorobiphenyl.

(^{31}P) $y = 22574x - 25268$, $R_2 = 0.9997$, (^{32}S) $y = 7303x - 10429$, $R_2 = 0.9993$, (^{35}Cl) $y = 681x$, $R_2 = 0.9961$.

As can be seen, the calibration curves have almost the same slope in comparison with the curves obtained by external calibration, which indicates that the elemental response is independent of the used species.

Using CIC concentrations of 32.69 μg L^{-1} (^{31}P), 32.21 μg L^{-1} (^{32}S) and 30.52 μg L^{-1} (^{35}Cl) was calculated for the Chlorpyrifos content of the tomato extract. These results are also in good agreement with the data found by GC-MS and external calibration GC-CC-ICP-MS.

The concentrations of the other compounds identified in the extract were also calculated by CIC: Ethoprop 6.25 μg L^{-1} (^{31}P), Fensulfothion 9.84 μg L^{-1} (^{31}P), 7.71 μg L^{-1} (^{32}S), Dildrin 21.58 μg L^{-1} (^{35}Cl), Mirex 11.08 μg L^{-1} (^{35}Cl).

Unfortunately, only the Chlorpyrifos content of the tomato extract has been quantified by GC-MS so a further comparison of the other compounds is not possible.

Besides the identified compounds the chromatogram of the tomato extract indicates some more peaks which do not match with any of the known retention times.

To identify some more compounds retention-time locking has been applied by locking the retention time of chlorpyrifos-methyl to those given in a pesticide database supplied with the Agilent GC system and which has been obtained with the same HP5-MS column. Therefore, the retention time of chlorpyrifos-methyl at different column-head pressures has been measured. The resulting graph can be described as $y = 0.0088x^2 - 0.6576x + 25.508$.

For locking the retention time of chlorphyrifos-methyl to those given in the database a calculated column-head pressure of 20.94 psi was necessary, resulting in a retention time of 16.603 ± 0.006 min ($n = 6$). In comparison with the expected retention time (16.596 min) an RSD of 0.04% has been obtained.

Table 6 shows a comparison of the retention times of the detected compounds in the tomato extract under locked conditions and the data obtained from the GC database.

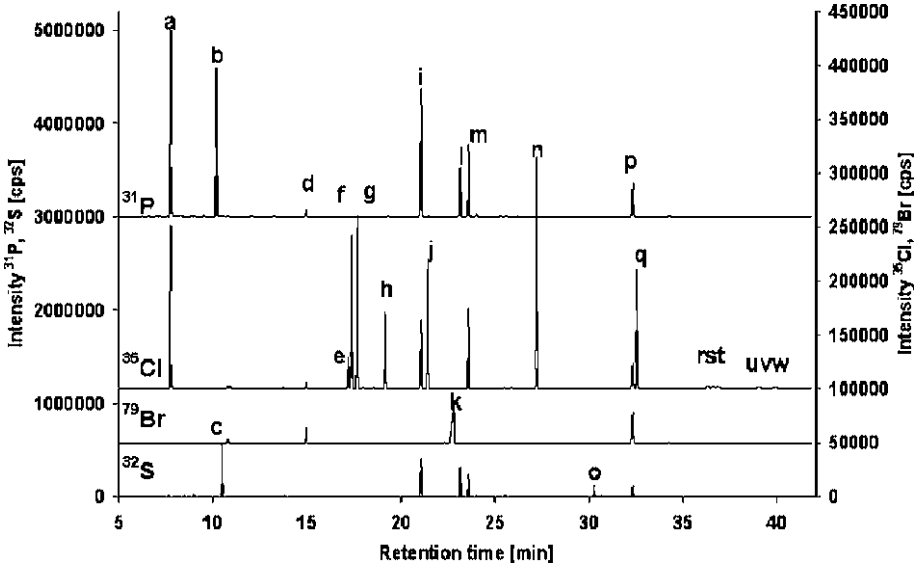

Fig. 6 Well resolved separation and heteroelement-specific detection of a pesticide mixture containing 23 compounds (1 μL pulsed splitless injection) by GC-ORS-ICP-MS. Peaks could be assigned by their retention time as: a, Dichlorvos; b, Mevinphos; c, Venolate; d, Dibrom "naled"; e, Atrazin; f, BHC beta isomer; g, Lindane; h, Chlorothalonil; i, Chlorphyrifos methyl; j, Heptachlor; k, Bromacil; l, Malathion; m, Chlorpyrifos; n, *p,p'*-DDE; o, Propagite; p, Leptophos; q, Mirex; r, Cypermethrin I; s, Cypermethrin II; t, Fenvalerate I; u, Fenvalerate II; v, Fluvalinate-tau-I; w, Fluvalinate-tau-II.

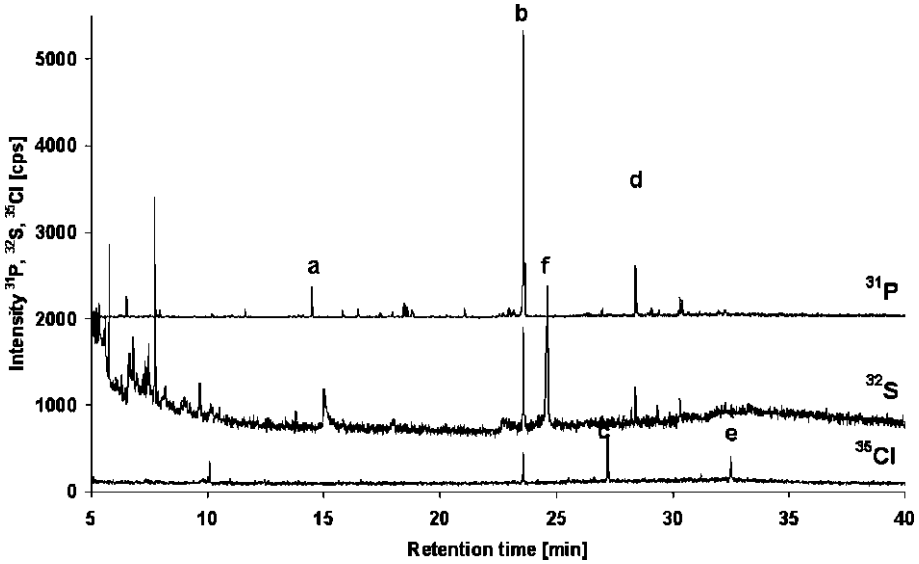

Fig. 7 Separation and element-specific determination of pesticides in a tomato extract by GC-ORS-ICP-MS. Peaks could be assigned as: a, Ethoprop; b, Chlorpyrifos; c, Dildrin; d, Fensulfothion; e, Mirex; f, sulfur (S_8).

Table 6 Pesticide identification in an tomato extract by retention time and comparison with database results

		Retention time/min					
Compound	Formula	^{31}P	^{32}S	^{34}S	^{35}Cl	Database	RSD (%)
Ethoprop	$C_8H_{19}O_2PS_2$	10.84				10.74	0.93
Chlorphyrifos	$C_9H_{11}Cl_3NO_3PS$	19.21	19.20	19.20	19.21	19.23	0.1
Sulfur (S_8)	S_8		19.89	19.89		20.02	0.65
Dieldrin	$C_{12}H_8Cl_6O$				23.61	23.76	0.46
Fensulfothion	$C_{11}H_{17}O_4PS_2$	25.31	25.31	25.31		25.56	0.94
Mirex	$C_{10}Cl_{12}$				29.64	29.84	0.67

One further peak could be identified as sulfur (S_8) which is commonly used as an acaricide and fungicide. The retention times of the other compounds which are already identified were also in good agreement with the retention times given in the database. For the future it will be necessary to improve the accuracy and therefore also the reliability of the database based pesticide identification.

By using retention-time looking (RTL) for compound identification, the number of detectable compounds is only limited by the complexity of the database and the resolution of the chromatographic separation.

Conclusions

GC hyphenated with collision cell ICP-MS represents a sensitive and highly selective alternative for the simultaneous determination of phosphorus, sulfur, chlorine, bromine and iodine containing pesticides either in mixed standard samples or in fruit extracts by performing only one chromatographic separation.

Due to the multi-element capability of the instrumental setup and the good accuracy of the retention times that were achieved, identification of the detected pesticides can be carried out using their retention times, the element compositions and element ratios present in each chromatographic peak.

In combination, optimisation of different instrumental parameters such as plasma conditions, collision cell settings, lens settings or application of additional plasma gases, drastically increased the overall sensitivity of the described methodology.

Quantification of the compounds detected could either be carried out by external calibration or compound independent calibration with comparable results. Future application of retention time locking (RTL) for compound identification and compound independent calibration for quantification could increase significantly the number of compounds identified by the setup used without using standards for all possible compounds. The number of detectable compounds is only limited by the chromatographic separation efficiency and the availability of retention time data for peak assignment.

The use of, for example, sulfur/phosphorus pesticides which contain enriched sulfur isotopes, and the isotope dilution technique, could help to further increase the accuracy of the GC-ICP-MS setup.

Overall, the proposed setup offers the possibility of using GC-ICP-MS for rapid screening of hetero-element containing compounds such as pesticides in an environmentally relevant sample matrix.

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