

Ion mobility spectrometry of laser desorbed pesticides from fruit surfaces

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Abstract The applicability of a technique combining laser desorption and ion mobility spectrometry for rapid detection of pesticides on fruit surfaces is explored. A selection of 20 fungicides, herbicides and insecticides with very different chemical and spectroscopic characteristics was used to study its features. For a variety of fruits the maximum tolerable laser irradiance was determined, at which no signals are generated by the clean surface. The spectra recorded for each substance on fruits were compared to those obtained for the same compound using laser desorption from a well defined surface. Furthermore, the influence of a dew layer on the sample was investigated. Limits of detection were estimated to be in the range of some tens of ng/kg for apples.

Keywords Pesticides · Food analysis · Laser desorption · Ion mobility spectrometry

Introduction

Adequate supply of the world's growing population with food is unthinkable without the benefits of modern agriculture including the use of a broad variety of chemicals for fertilization and plant protection. On the other hand many of the substances used in fruit and vegetable production are at

least suspected to cause a threat to human health and consumers have to be protected from contact with them. In particular insecticides, fungicides and herbicides commonly summarized by the term pesticides are a matter of intense discussion in this context [1]. Consequently monitoring of pesticide residues is a fundamental component within the efforts to insure food safety and keep in compliance with extensive national and international regulations [2]. Sophisticated analytical techniques based on chromatographic separation coupled to mass spectrometry or other detectors exist which allow for the detection and quantification of pesticides with extremely high sensitivity [3]. However, all of them require sample preparation steps and are characterized by long measurement durations and limited sample throughput. The results of such an analysis are usually available not before the food is either consumed or rotten. Clearly, these methods are not suitable for a monitoring system aimed to guarantee unpolluted fruits and vegetables for the consumer.

Regarding the variety of analytical instrumentation and procedures for pesticide residue analysis it becomes obvious that there exists a lack of rapid screening methods that allows for the identification of contaminated food in real time on its way from the producer to the consumer. Due to the large number of pesticides and their varying physical and chemical features such a technique should be applicable to the analysis of very different groups of chemicals. Furthermore, the food examinations are to be carried out on-site in the rather harsh environment of a storehouse etc. by unspecialized personnel. These boundary conditions demand for a robust and easy to operate instrument requiring only a minimum of supplies and service. Several approaches to solve this problem can be found in the literature [4–6]. However, a commercial device is not yet available. Reasons for this dilemma may be found in the broad variety of physical and chemical features exhibited by the substances

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used in plant protection, in the varied matrices fruits and vegetables represent and in the small concentrations at which pesticides have to be detected in food.

Recently we suggested a combination of laser desorption [7–10], and ion mobility spectrometry [11, 12], for fast screening of fruit and vegetable surfaces in respect to pesticide residues and presented the results of a practicability study [13]. As these results were rather promising the method was further investigated and optimized. In particular the poor limits of detection and the insufficient separation power of the differential mobility spectrometer used in the first studies were counteracted by replacing it by a drift time instrument. Moreover, the method was tested for a larger number and broader variety of substances and the influence of the fruit surface and its humidity on the measurement results were investigated. The results of these studies are presented in the paper at issue.

Experimental

The setup for the investigations reported here is sketched in Fig. 1 and was built around a commercial ion mobility spectrometer (Sensortechnik und Elektronik Pockau GmbH, Pockau, Germany) based on an IMS cell with a length of 5 cm, an inner diameter of 10 mm and equipped with a tritium ion source with an activity of ca. 50 MBq. Cations are injected into the drift region by means of a 400 V pulse with a duration of 60 μ s. The drift gas (flow ca. 400 ml min^{-1}) and the carrier gas are supplied by a pump which transports

air from the IMS drift cell through a filter and a flow splitter. In order to obtain fast response of the instrument and to avoid memory effects all valves were removed from the gas circulation system and the IMS cell heated to 80 °C.

For laser desorption of adsorbed material the surface under investigation was pressed manually onto the 5 mm orifice of a homebuilt desorption cell made of brass. The top of the cell was covered with a fused silica window through which the laser beam entered the cell, passed through it and irradiated the sample pressed onto the bottom. For laser desorption the output of a frequency quadrupled Nd:YAG-laser (Minilite II, Continuum, Santa Clara, CA) operating at a wavelength of 266 nm and delivering pulses of up to 6 mJ energy and ca. 5 ns duration was used. The laser beam was guided to the sample by means of a dielectric mirror and irradiated a spot of ca. 3 mm diameter. Desorbed material was flushed into the IMS ion source located ca. 5 cm from the desorption cell through a PTFE tube with an inner diameter of 2 mm. The air flow through the desorption cell was adjusted to 160 ml min^{-1} .

All pesticides measured were analytical standards (>99% purity) and were obtained from Riedel-de-Haën (Seelze, Germany). The compounds investigated are summarized in Table 1. Substances were chosen which are widely used particularly in the production of apples and are frequently found in pesticide residue analysis. Furthermore, the examples represent various groups of chemicals (e.g. organophosphorous pesticides, pyrethroids, carbamates) and different areas of application (insecticides, fungicides, herbicides).

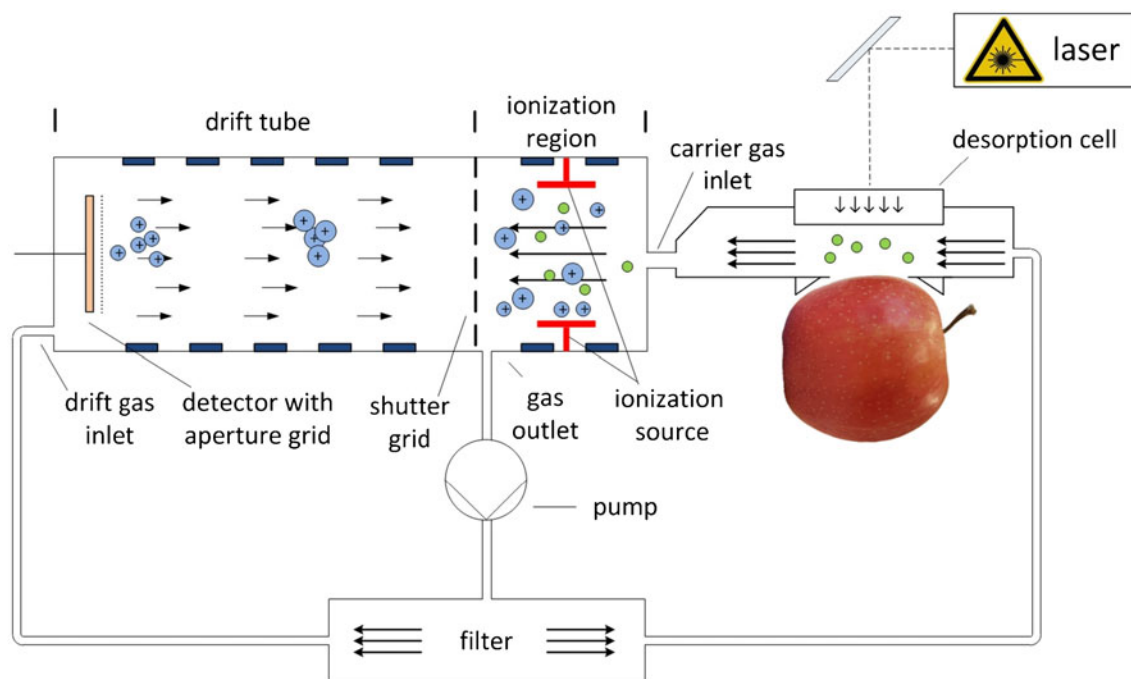


Fig. 1 Experimental setup for pesticide detection on fruits comprising an ion mobility spectrometer with tritium ion source and a laser desorption device

Table 1 List of the pesticides investigated in this study and their behaviour in laser desorption ion mobility spectrometry when analyzed on paper and on an apple surface respectively. The quality of the spectra obtained is classified according to the following features: a: single characteristic peak, b: several, but characteristic peaks, c: broad and unstructured signal, d: no detectable signal

Pesticide	CAS number	Molecular formula	Molecular weight g/mol	signal quality
Acetamiprid	160430-64-8	C ₁₀ H ₁₁ CIN ₄	222,68	b
Azoxystrobin	131860-33-8	C ₂₂ H ₁₇ N ₃ O ₅	403,40	b
Boscalid	188425-85-6	C ₁₈ H ₁₂ Cl ₂ N ₂ O	343,21	a
Captan	133-06-02	C ₉ H ₈ Cl ₃ NO ₂ S	300,59	a
Cyprodinil	121552-61-2	C ₁₄ H ₁₅ N ₃	225,30	a
Difenoconazole	119446-68-3	C ₁₉ H ₁₇ Cl ₂ N ₃ O ₃	406,30	b
Dimethoate	60-51-5	C ₅ H ₁₂ NO ₃ PS ₂	229,30	b
Dithianon	3347-22-6	C ₁₄ H ₄ N ₂ O ₂ S ₂	296,30	d
Fenhexamid	126833-17-8	C ₁₄ H ₁₇ Cl ₂ NO ₂	302,20	a
Fenoxycarb	79127-80-3	C ₁₇ H ₁₉ NO ₄	301,34	d
Fludioxonil	131341-86-1	C ₁₂ H ₆ F ₂ N ₂ O ₂	248,19	c
Indoxacarb	173584-44-6	C ₂₂ H ₁₇ ClF ₃ N ₃ O ₇	527,84	b
Iprodione	36734-19-7	C ₁₃ H ₁₃ Cl ₂ N ₃ O ₃	330,17	b
Mepanipyrim	110235-47-7	C ₁₄ H ₁₃ N ₃	223,27	c
Myclobutanil	88671-89-0	C ₁₅ H ₁₇ CIN ₄	288,78	b
Pirimicarb	23103-98-2	C ₁₁ H ₁₈ N ₄ O ₂	238,29	b
Pyraclostrobin	175013-18-0	C ₁₉ H ₁₈ CIN ₃ O ₄	387,82	b
Quinoxifen	124495-18-7	C ₁₅ H ₈ Cl ₂ FNO	308,14	a
Spirodiclofen	148477-71-8	C ₂₁ H ₂₄ Cl ₂ O ₄	411,32	a
Thiacloprid	111988-49-9	C ₁₀ H ₉ CIN ₄ S	252,73	b

Fruits were either picked in one of the author's garden or purchased from a local supermarket. Before use in the experiments the fruits were checked for an already existing pesticide contamination using the laser desorption IMS procedure described here. When no background signal from the untreated surface could be detected (which was the case for all samples) the fruit was considered as clean. For the following measurements the fruits were contaminated with a pesticide by touching them with a paper towel on which a few pulverized crystals of the substance were distributed over an area of about 1 cm². According to the number and size of the crystals the amount of pesticide on the towel was estimated to be a few nanograms. The amount of pesticide actually transferred onto the fruit surface could not be determined.

Results and discussion

In a first step, the ion mobility spectrum of each pesticide listed in Table 1 was recorded. In order to minimize matrix effects the individual substances were prepared in solid form on clean bleached paper and laser desorbed from there. The same paper was used to contaminate the fruit surfaces by touching a small area of the fruit with it. Afterwards the fruit was analyzed in the same way as the piece of paper.

Figure 2 shows some typical results obtained in these investigations. In any case the spectra observed for an

individual substance when laser desorbed from paper a similar spectrum was observed for the fruit surface contaminated with this pesticide. Obviously, for the compounds used in this study the laser desorption process is not significantly affected by the surface type.

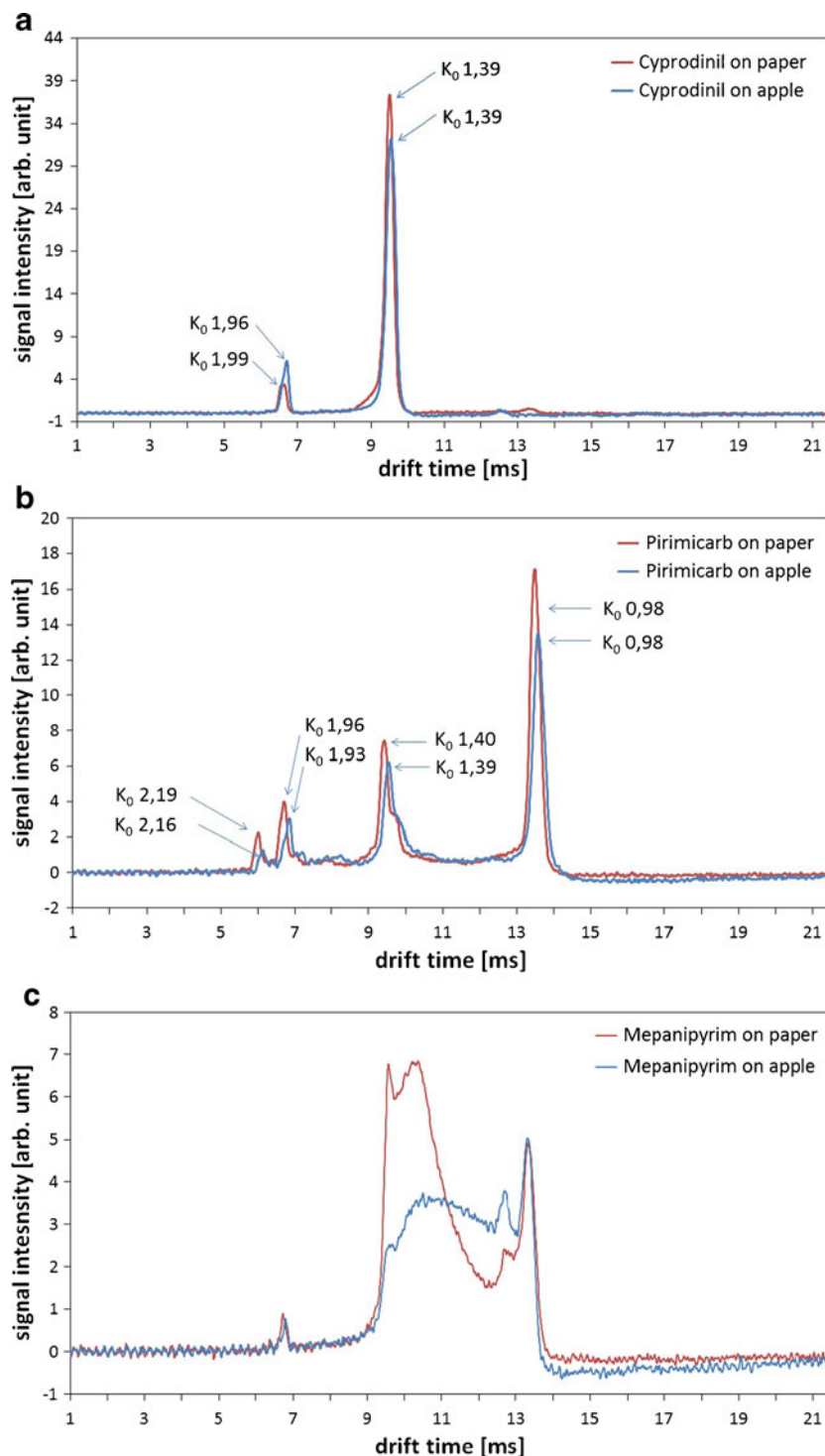
A first group of compounds delivered a single characteristic peak in the laser desorption IMS measurements. The spectrum obtained for Cyprodinil is shown in Fig. 2a as an example.

For a few substances more than one peak could be observed in their IMS spectra, as in the example shown in Fig. 2b. The additional signals may be assigned to clusters or fragments produced either by the laser desorption process or by thermal decomposition in the heated ion mobility spectrometer.

Only broad and unstructured signals were observed for a third group of pesticides in laser desorption IMS. An example is shown in Fig. 2c. The reason for this remains unclear but may be found in efficient water cluster formation of these compounds or in other ion molecule reactions. In order to gain insight into these processes and to overcome the problems connected with them it is desirable to test other ionization methods in particular single photon ionization by means of vacuum ultraviolet radiation.

In certain cases it was not possible to generate any usable laser desorption ion mobility spectrum for the pesticide under investigation. The question whether the reason for this can be found in the laser desorption step or in the IMS

Fig. 2 Ion mobility spectra of individual pesticides laser desorbed from paper and an apple skin respectively. **a** Example of a spectrum with a single characteristic peak (Cyprodinil), **b** example of a spectrum with several but still identifiable peaks (Pirimicarb), **c** example of an unstructured spectrum (Mepanipyrim)



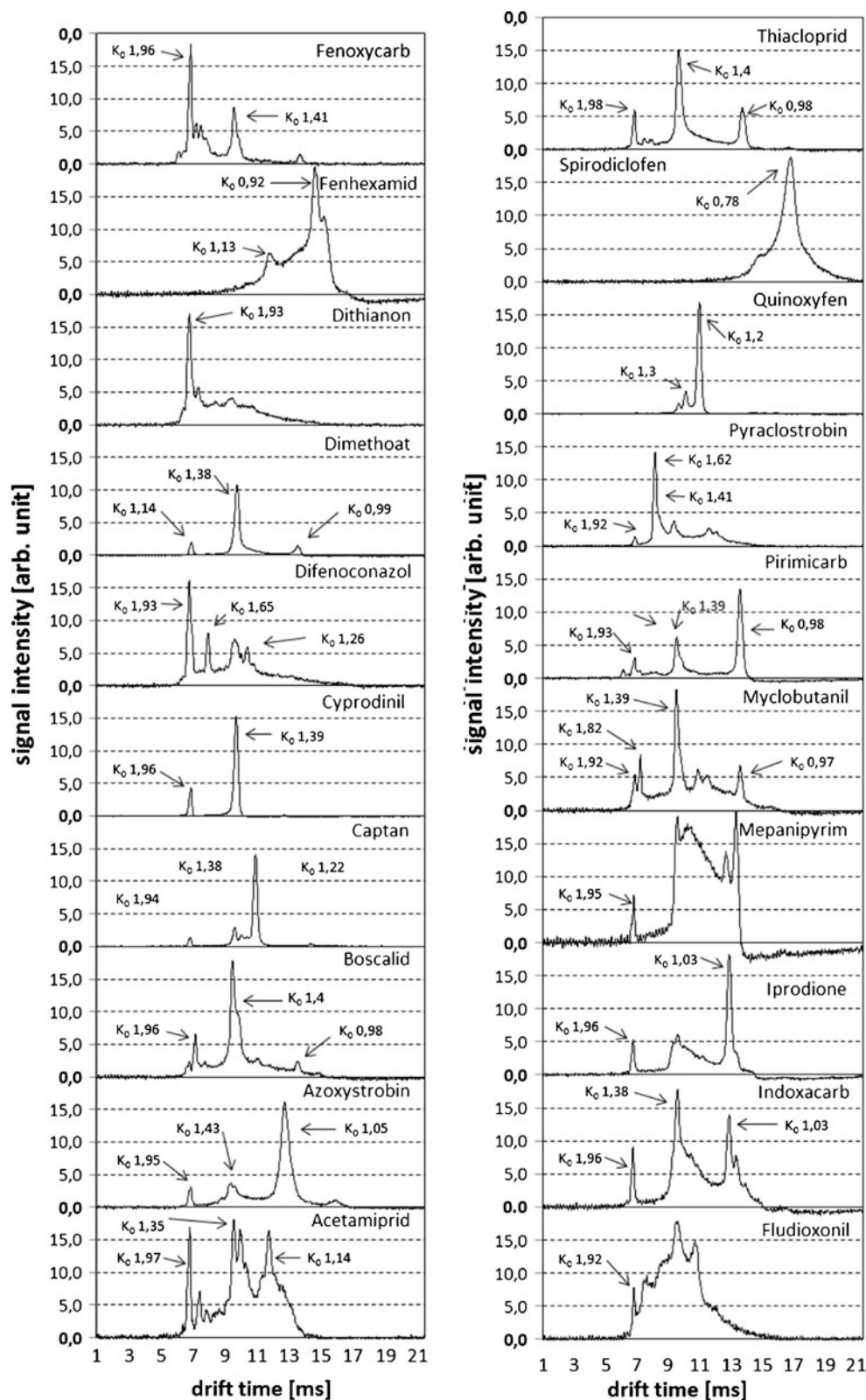
detection could not be answered on the basis of the experimental setup employed in these studies.

The last column of Table 1 indicates to which group of compounds each pesticide investigated belongs and Fig. 3 displays the ion mobility spectrum of each substance.

In order to achieve efficient laser desorption of pesticides on a fruit surface sufficiently high laser intensities should be applied. On the other hand the laser intensity should be kept

low enough to minimize signals from an uncontaminated surface in order to avoid interference problems. Therefore, the signals of several untreated fruit surfaces irradiated with increasing laser intensity were recorded. In all cases summarized in Table 2 the signals of the reactant ions started to decrease above a certain value of the irradiance. The laser intensity which resulted in a reduction of the reactant ion peaks by 20% is given in the second column of Table 2.

Fig. 3 Laser desorption ion mobility spectra of the pesticides investigated in this work.



However, this irradiance did not lead to the observation of additional peaks in the drift time spectrum. For some fruits it was possible to generate signals emerging from the untreated fruit skin by a further rise of the laser intensity. Figure 4

shows the development of the ion mobility spectra obtained by laser irradiation of an apple (a) and a white grape (b) while increasing the irradiance. As a primary effect a reduction of the reactant ion signal can be observed starting at

Table 2 Laser intensity on uncontaminated fruit surfaces resulting in a 20% reduction of the reactant ion peaks. This value of the irradiance should not be significantly exceeded in order to avoid matrix signals

Fruit/ vegetable	Laser irradiance [MW/cm ²]
Plum	0,33
Peach	4,2
Grape	2,6
Tomato	2,0
Apple	2,7

about half of the maximum irradiance. Simultaneously, in the low drift time range (<8 ms) additional signals are emerging which are due to components of the fruit skin. However, the drift time range in which the pesticides studied in this work are detected remains free of interfering matrix signals.

The laser desorption IMS experiments described above did not allow for a quantitative determination of the desorbed material. Thus, it was not possible to determine limits

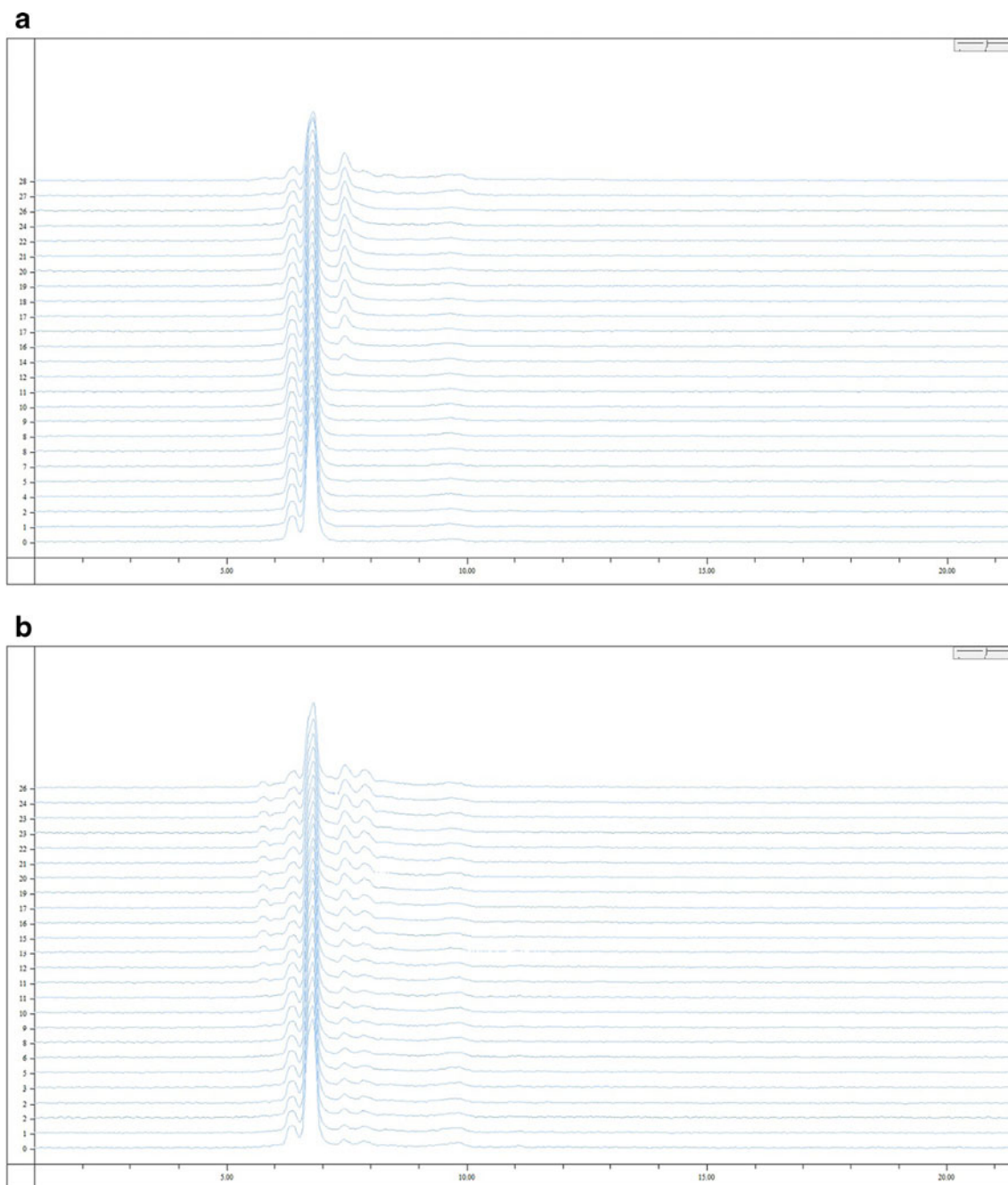


Fig. 4 Development of laser desorption ion mobility spectra when increasing the irradiance from zero to a maximum of 18,2 MW/cm² obtained for uncontaminated fruits: **a** apple, **b** white grape

of detection for the target substances and the sensitivity of the technique in this way. The major problem in this context arises from the difficulty to produce pesticide layers with a well defined surface concentration on the fruits. However, an upper limit of an LOD may be estimated by using the value for the amount of pesticide transferred onto the fruit surfaces. Assuming that about one nanogram of pesticide was distributed over ca. 1 cm^2 of apple skin this corresponds to a total of 154 ng for an apple of diameter 7 cm in case of a homogeneous covering. Related to the fruit's mass, this results in a concentration of 855 ng/kg. Considering the facts that the signal intensities observed in these measurements are at least ten times above the required minimum, it can be concluded that the detection limit of the current apparatus will be in the range of some tens of ng/kg. A major drawback of this apparatus can be found in the fact that only a single surface spot was analyzed. A future instrument will overcome this problem by scanning the laser beam over the fruit surface in order to analyze numerous individual points. Besides improving the statistical quality of the results this measure in addition will also help to improve the overall sensitivity of the method.

Finally, the influence of a water layer that may cover a fruit was investigated. Water is a main constituent of every fruit and in addition a water layer may cover its surface as a result of rain or condensation. As the water concentration in the sample gas is known to have an effect on IMS measurements [14, 15], the results obtained for untreated fruit surfaces and the detection of a contaminant were compared for the two cases of a rather dry surface and one covered with dew. In order to achieve a comparatively dry skin the fruit was slightly warmed up above room temperature and kept at elevated temperature for ca. 5 min. A dew layer was produced by cooling the fruit to $8 \text{ }^\circ\text{C}$ and then exposing it to the ambient air with a relative humidity of ca. 60% for ca. 5 min.

For the dry as well as for the wet surfaces of untreated fruits the irradiance was determined at which a change in the

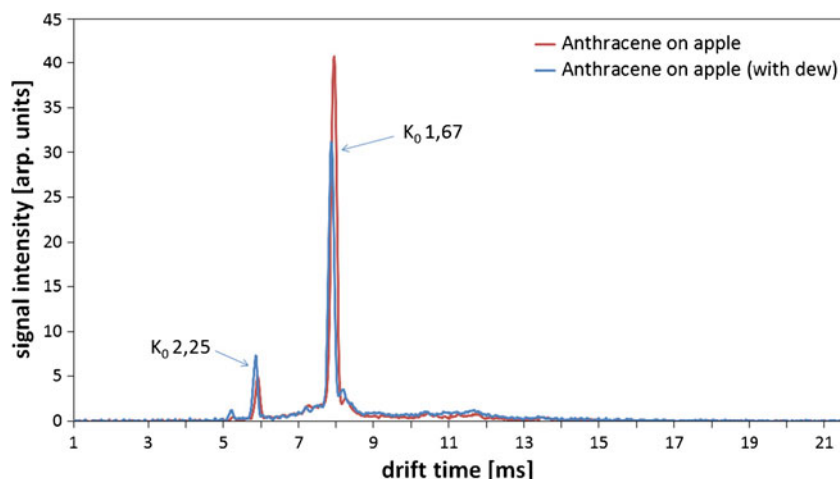
IMS spectrum was observed and spectra at significantly high laser intensities were recorded in the same way as described above. In these experiments no differences could be observed between the fruit skins with and without water covering. A possible effect of the surface humidity on the detection of a contaminant was investigated using an apple treated with anthracene. It could easily be identified on the warm and dry apple skin but was found using the same laser parameters with comparable signal intensity on the cold and humid surface as well. Figure 5 compares the ion mobility spectra obtained for those two cases. These observations could be explained assuming that water on the surface is removed by laser irradiation. Due to the high irradiance this is likely although the absorption coefficient of liquid water only poses a moderate value at a wavelength of 266 nm [16]. In this model the laser light acts as a drier and removes the water layer while its intensity is increased. Independent of the surface humidity non-volatile contaminants are then always desorbed from a "dry" surface.

Conclusion

The investigations carried out so far demonstrate that the combination of UV laser desorption and ion mobility spectrometry has the potential to rapidly detect rather different types of pesticides on a variety of fruit surfaces. The detection limits that can be achieved with such a hybrid instrument are supposed to be found in the actually required ng kg^{-1} range and are therefore sufficient.

Particular emphasis was laid on the test of the method's features under realistic conditions, i.e. for a variety of fruits and different skin humidity. The primary observation in this context is the broad spread of laser intensity leading to an onset of interfering IMS signals when different sorts of fruits are investigated. Consequently, the laser irradiance and the duration of the irradiation have to be carefully

Fig. 5 Comparison of the laser desorption ion mobility spectrum obtained for dry apple skin contaminated with anthracene with that recorded for a similarly treated apple but covered with dew



adjusted for every individual fruit type in order to avoid matrix interference problems while still maintaining efficient laser desorption.

It is a problematic point of the analytical method described here to obtain quantitative information about the substances detected on a surface. This is due to the fact that it involves several processes with unknown efficiencies, e.g. the laser desorption process, the transmission of the desorbed material into the IMS and the detection efficiency within it. While the IMS is a rather stable instrument whose long term drift can be recognized and taken into account by measuring a volatile standard added to the sample gas prior to the actual measurements, laser desorption is a statistical process by itself, e.g. due to short term fluctuations of the laser pulse energy. In order to minimize these effects a further developed version of our instrument utilizes a motor driven mirror which allows scanning the laser beam over a predefined area of the fruit skin. One hundred individual spots are irradiated within 10 s giving rise to an averaged signal which then is almost independent of laser pulse-to-pulse fluctuations and resembles the contamination of a much larger part of the fruit surface than a single spot measurement. In addition, long term drifts of laser parameters can be controlled by monitoring the beam with a suitable instrument.

The method presented here was tested using the group of 20 pesticides listed above. However they represent only about 1% of the chemicals used in plant protection nowadays. Even within this group the detection of some compounds was problematic and further investigations particularly in respect to ionization techniques have to be carried out in order to overcome them. Therefore, the current status does not allow to consider the combination of laser desorption and ion mobility spectrometry a generally applicable technique for pesticide analysis. Although we chose pesticides which from the chemical and spectroscopic point of view are rather divers, only the experience gained in field test with potential users and under realistic conditions

will be able to show whether this method is able to cover a large enough portion of the substances in use. This work is on its way and will help to further optimize the method presented in this paper.

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