Selective Determination of Dimethoate Using Ion Mobility Spectrometry with Single and Mixed Alternate Reagent Ions

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Dimethoate, one of the organophosphorus pesticides, was selectively determined by ion mobility spectrometry (IMS) along with the single and mixed alternate reagent ions. By doping ammonium, acetone, ethanol, ether, and methanol into the carrier gas, the best selective detection was obtained by the addition of ammonium having the highest proton affinity among these single alternate reagent ions. Three mixed alternate reagents including ammonium−acetone, ammonium−ether, and acetone−ether, which were also used to improve the selectivity, showed better results than that single-solvent dopants gained. The best resolution and the highest abundance of the dimethoate peak were observed in its IMS spectrum after the addition of the mixed ammonium−acetone among all the above-mentioned dopants. The relationship curves for the concentration of ammonium and mixed ammonium−acetone to the response of dimethoate were studied. Ammonium at ∼1.0 µg/L levels or 1.0 µg/L ammonium at plus acetone at ∼1.0 µg/L levels exhibited the strongest response of dimethoate. In addition, the direct determination of dimethoate residues was compared to its selective detection with mixed ammonium−acetone as the alternate reagent ions in a field test. A model for the selective analysis of an analyte having middle proton affinity in mixed compounds is proposed.

Ion mobility spectrometry (IMS) is a sensitive analytical technique for the detection of volatile organic compounds (VOCs) at low concentration. It plays an important role in practical applications such as industrial and environmental monitoring and drug and explosives detection.[1]

Due to the low minimum detectable limits (MDLs) of IMS and its response to numerous organic functionalities, the ion mobility spectra are complicated by matrix effects if the analyte is an actual sample or the instruments are operated under conditions of general response, i.e., with water reagent gas chemistry; thus, a solution to minimize the matrix effects is necessary. Ammonium, acetone, and halide ions were used as alternate reagent ions to improve the selectivity of some compounds under the positive and negative operation modes, respectively.[2−5] The reason is that

these ions have high proton affinities or electron affinities; only those compounds of proton affinities or electron affinities higher than the three ions can be selectively ionized and detected; thus, the response intensity and resolution of the analytes can be improved. The subject of alternate reagent ion chemistry in IMS has been an interesting research topic in our laboratory[6] and with other groups.[2−5]

Although ion mobility spectrometric studies of organophosphorus compounds (OPCs) have been reported,[5,7−9] they mainly discussed the correlations among the masses, structures of the ions formed, and their mobilities. An excellent report by Eiceman et al. only described the application of single alternate reagent gases for the selective analysis of 45 VOCs and 19 OPCs. In our experiment, single and mixed solvents of different proton affinities were used as the alternate reagents for the selective detection of dimethoate. Dimethoate is an organophosphorus systemic insecticide, which is applied widely in agriculture and forestry in China to control the damage from pests. The environmental pollution caused by such applications is serious. It is important to monitor the residues of dimethoate in the field for the purpose of environmental protection. The conventional methods to determine dimethoate residues in vegetables, fruits, waters, and soil are gas chromatography with a nitrogen−phosphorus detector and liquid chromatography with a mass-selective detector.[10−12] However, it is difficult to monitor the residues of dimethoate in air by these methods. The wide applications of IMS to other OPCs in the past present its potential application in monitoring dimethoate.

Dimethoate is complex structure and a lot of peaks may appear in its general IMS spectrum, resulting in weak response and low resolution of the principal component peak. Therefore, the alternate reagent ions were attempted in our experiment to enhance the selectivity of the detection of dimethoate.

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Table 1. Constituents and Their Proton Affinities in 40% Emulsifiable Dimethoate

	proton affinity (ev)
ethane	6.2
benzene	8.2
methylbenzene	8.5
dimethylbenzene	8.7
organophosphorus compound	9.4

Except for the use of the single alternate reagent gases, the first application of mixed alternate reagent gases that are composed of two solvents was studied here and showed results better than single solvents did. The relationship curves between the concentrations of the best dopants in this test and the response of dimethoate were also studied. Finally, a new model for determining compounds whose proton affinities are intermediate in mixed compounds with several alternate reagent ions was proposed.

EXPERIMENTAL SECTION

An IMS-2000 ion mobility spectrometer (Spectrospin), made by Bruker Saxonia Analytik GmbH, was used in our laboratory. An IBM-compatible computer with math co-processor and software (Ion Mobility Spectrometer Version 3.0) was used for data acquisition. All the reduced mobility values in this paper are corrected by the reference compound 2,4-dimethylpyridine (lutidine), which gives a significant peak and a stable value (1.95 cm^2 V^{-1} s^{-1}) in the IMS spectrum.

Ammonium, acetone, ether, ethanol, methanol, and dimethoate were all commercially available (made in China) and were used without any further purification. The dimethoate was a 40% emulsifiable formulation. All organic solvents were analytical grade. The ambient air was used as the carrier gas, and the drift gas was prefiltered air which was drawn in through the zero gas filter (type 13× molecular sieve).

The instrument operation conditions are as follows: electric field, 297 V/cm; gate width, 0.3 ms; repetition rate, 30 ms; temperature of drift tube, 30 °C; typical pressure, 735 mmHg; flow rate of carrier and drift gas, 16.7 mL/min.

RESULTS AND DISCUSSION

The constituents in 40% emulsifiable dimethoate and their proton affinities are shown in Table 1. Initially an ion mobility spectrum of the headspace vapor of dimethoate was acquired under general conditions and is shown in Figure 1. Since the ambient air was the carrier gas, the main reactant ion was $(H_2O)_n$ H^+ of comparatively low proton affinity; thus, most components in dimethoate may form their product ions by proton-transfer reaction with the hydrated protons. The results of Figure 1 are described as follows: 2.25 and 2.12 cm^2 V^{-1} s^{-1} are the reactant ions, 1.78 cm^2 V^{-1} s^{-1} may be the peaks of benzene, 1.39 cm^2 V^{-1} s^{-1} may be the peak of dimethylbenzene, 1.54 cm^2 V^{-1} s^{-1} may be the monomer peak of dimethoate, and 1.26 cm^2 V^{-1} s^{-1} may be the protonated dimer ion peak of dimethoate. The peaks of Figure 1 and other figures in this paper were assigned and verified by the addition of the standard compounds of each individual components. Evidently, it is difficult to determine the dimethoate under matrix effects in such a low-resolution spectrum.
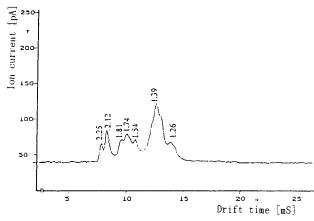
Figure 1. The ion mobility spectrum of the headspace vapor of dimethoate. (Peaks at 2.25 and 2.12 cm^2 V^{-1} s^{-1} are the reactant ions, 2.07 and 1.74 may be the peaks of benzene, 1.81 is the peak of methylbenzene, 1.39 may be the peak of dimethylbenzene, 1.54 may be the peak of the monomer ion of dimethoate, and 1.26 is the protonated dimer ion peak of dimethoate.)

Table 2. Five Solvents and Their Proton Affinities

solvent	proton affinity (ev)
acetone	8.7
ammonium	9.1
ethanol	8.4
methanol	8.2
ether	8.9

The above result is probably attributed to the following. During the process of atmospheric ionization, the average free distance is very short, a lot of ion−molecular reactions may occur in the reaction region, and the thermodynamic balance and chemical balance can be built up rapidly. The product ions are formed by competitive ion−molecule reactions such as collisional charge exchange; the final product ions depend on the relative ionized energy, proton or electron affinities, and concentration of the individual compounds in the gas phase of the ion source. In vaporized emulsifiable dimethoate, components such as benzene, methylbenzene, and dimethylbenzene, which are easy to vaporize, occupy almost all the volume of the gas sample. These molecules can be ionized by the transfer reactions with reagent ions that exist in the ion source and appear in the spectrum if ambient air is used as carrier gas. The very low volatility of dimethoate results in limited amounts of dimethoate molecules in gas sample, thus a weak response and low-resolution peak. Other peaks of Figure 1 make it complicated and ambiguous to resolve the principal component. Consequently, it is necessary to find a way to eliminate the interferences from other constituents and detect the dimethoate selectively, which will be described in detail in the following sections.

1. Ion Mobility Spectra of Dimethoate Along with Different Single Dopants and Their Selective Effects. Five solvents of different proton affinities were added into the carrier gas and used as the alternate reagent ions. These solvents and their proton affinities are shown in Table 2. Under the identical operational conditions, the drift times and ion mobilities of the individual standard compounds of these solvents were determined and are shown in Table 3.

Table 3. Ion Mobilities and Drift Times of Five Solvents

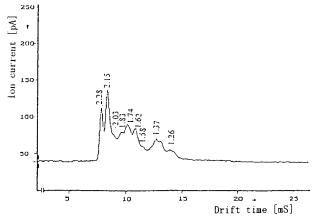| solvent	drift time (ms)	ion mobilities (cm^2 V^{-1} s^{-1})
acetone	9.49	1.82
ammonium	7.63	2.26
ethanol	9.44	1.83
methanol	8.45	2.04
ether	9.88	1.74

Figure 2. The ion mobility spectrum of dimethoate with methanol dopant. (Peaks at 2.28, 2.15, and 2.03 cm^2 V^{-1} s^{-1} are the reactant ions, 1.62 is acetone product ions, 1.83 is methylbenzene product ion, 1.74 is the dimer ion of benzene, 1.58 is the monomer ion of dimethoate, 1.37 is dimethylbenzene product ion, and 1.26 is the dimer ion of dimethoate.)

Figure 3. The ion mobility spectrum of dimethoate with ethanol dopant. (Peak at 2.03 cm^2 V^{-1} s^{-1} is the benzene product ion, 1.83 is the ethanol reactant ion, 1.78 is the methylbenzene ion, 1.64 is the clustered ion of acetone, 1.57 is the monomer ion of dimethoate, 1.36 is the dimethylbenzene ion, and 1.26 is the dimer ion of dimethoate.)

Figure 4. The ion mobility spectrum of dimethoate with acetone dopant. (Peaks at 1.86 and 1.62 are the acetone clustered ions, 1.54 is the monomer ion, 1.39 is dimethylbenzene, and 1.26 is the dimer ion of dimethoate.)

The ion mobility spectrum of dimethoate with methanol is shown in Figure 2. Although new reactant ions $(CH_3OH)_2H^+$ and $(CH_3OH)_2H^+(H_2O)$ were formed after the addition of methanol, their relatively low proton affinities were not helpful in eliminating the matrix effects arising from most of the constituents in dimethoate and almost all the peaks of these constituents were observed in the spectrum. The assignments of the peaks in Figure 2 were also determined by the standard addition methods. Peaks at 2.15 and 2.03 cm^2 V^{-1} s^{-1} are the reactant ions, 1.62 is the acetone product ion, 1.83 is the methylbenzene product ion, 1.74 is the dimer ion of benzene, 1.58 is the monomer ion of dimethoate, 1.37 is the dimethylbenzene product, and 1.26 is the dimer ion of dimethoate. As the alternate reagent ion for the analysis of dimethoate, methanol could not reduce the matrix effects and improve the selectivity of dimethoate.

Ethanol was added into the carrier gas, and the IMS spectrum was collected (Figure 3). The peak at 2.03 cm^2 V^{-1} s^{-1} is the benzene product ion,1.83 is the ethanol reactant ion, 1.78 is the methylbenzene ion, 1.64 is the clustered ion of acetone, 1.57 is the monomer ion of dimethoate, 1.36 is the dimethylbenzene ion, and 1.26 is the dimer ion of dimethoate. The effect is almost the same as methanol. The peak of dimethoate was still disturbed by other ion peaks except that its response was a little higher. Due to their lower proton affinities than most constituents in dimethoate, ethanol and methanol could not alleviate the interferences from other constituents and obtain the selective detection of dimethoate.

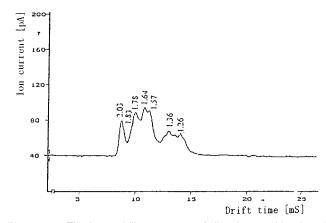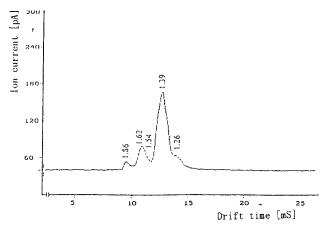The ion mobility spectrum of dimethoate with acetone is shown in Figure 4. Owing to the moderately high proton affinity of acetone, those constituents of lower proton affinities in dimethoate could not form their product ions by ion−molecular exchange reactions with new reactant ions. Only the peaks of dimethylbenzene and dimethoate were observed (1.54 cm^2 V^{-1} s^{-1} is the monomer ion peak of dimethoate, 1.39 is dimethylbenzene, and 1.26 is the dimer ion of dimethoate), but the response of dimethoate was still weak owing to its low volatility and the existence of dimethyl benzene. Charges mainly resided at dimethylbenzene, which is the principal solvent having moderately high proton affinity in emulsifier dimethoate. Acetone could not eliminate the interference from dimethylbenzene and was not an ideal dopant for dimethoate. The other two peaks at 1.86 and 1.62 in spectrum may be acetone ions.

The ion mobility spectrum of dimethoate with ether is shown in Figure 5. The interference from the constituents could not all be eliminated for the same reason as noted for acetone. The peak at 1.68 cm^2 V^{-1} s^{-1} is ether ion, 1.57 is the monomer peak of dimethoate, 1.37 is dimethylbenzene, and 1.26 is the dimer ion of dimethoate. The resolution and response of dimethoate are not satisfied under such a situation. Consequently, ether was not a suitable dopant as well.
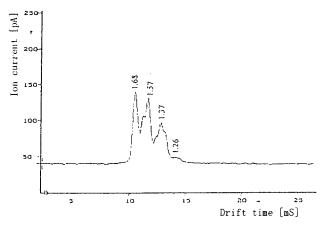
Figure 5. The ion mobility spectrum of dimethoate with ether dopant. (Peak at 1.68 is the ether ion, 1.57 is the monomer ion, 1.37 is dimethylbenzene, and 1.26 is the dimer ion of dimethoate.)
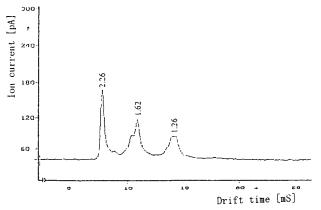

Figure 6. The ion mobility spectrum of dimethoate with ammonium dopant. (Peak at 2.26 is the ammonium reactant ion, 1.62 is the monomer ion, and 1.26 is the dimer ion of dimethoate.)

Figure 7. The ion mobility spectrum of dimethoate with ether and acetone. (Peak at 1.70 is the ether ion, 1.54 is the monomer ion, 1.37 is dimethylbenzene, and 1.24 is the dimer ion of dimethoate.)

Figure 8. The ion mobility spectrum of dimethoate with ether and ammonium. (Peak at 1.66 is the ether ion, 1.54 is the monomer ion of dimethoate, 1.39 is dimethylbenzene, and 1.24 is the dimer ion of dimethoate.)

The ion mobility spectrum of dimethoate with ammonium is shown in Figure 6. Only the clustered ion of ammonium (2.26 cm^2 V^{-1} s^{-1}), the monomer ion of dimethoate (1.62), and the dimethoate dimer ion (1.26) were observed in the spectrum; those compounds of proton affinities lower than ammonium were not found in the spectrum. When ammonium was added into the carrier gas and filled in the ion source, single reactant ion $NH_4^+(H_2O)_n$ was formed in the ion source; those compounds of lower proton affinities could not form their product ions by acquiring protons from such reactant ions. The resolution and response of dimethoate were enhanced for its proton affinity is higher than that of ammonium. The result shows that ammonium is a good dopant for dimethoate.

The order of the proton affinities of these above mentioned solvents is ammonium > ether > acetone > ethanol > methanol. Considered from the resolution and response abundance of the dimethoate peak obtained in those spectra, the selectivity of the determination of dimethoate is the best in ammonium and the worst in methanol, which is in accordance with the order of their proton affinities.

2. Ion Mobility Spectra of Dimethoate with Mixed Reagent Ions. The previous section and other papers[2−5] discussed the alternate reagent ion to eliminate or minimize the matrix effects in IMS measurements; however, only single alternate reagent ga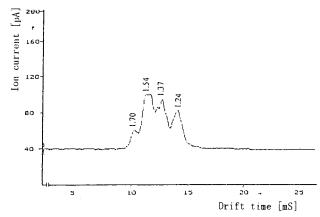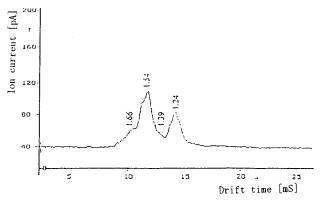s chemistry was adopted there. Mixed alternate reagents were first attempted for further enhancement of the selectivity in this paper.

The ion mobility spectrum of dimethoate with mixed acetone−ether is shown in Figure 7. Due to the close proton affinities between the two solvents and dimethylbenzene, the high-concentration solvents also gave their response under this situation, but the response of dimethoate was increased in a way. Such a mixed dopant is not well suited for the selective detection of dimethoate.

The ion mobility spectrum of dimethoate with mixed ether−ammonium is shown in Figure 8. Due to the existence of ammonium in the carrier gas, the response of dimethylbenzene decreased greatly and dimethoate was well resolved and gained a stronger response. The effect of selectivity is better than that of the former mixed dopant.

The ion mobility spectrum of dimethoate with mixed acetone−ammonium is shown in Figure 9. Since the reactant ions were exhausted in this spectrum, no reactant ion peaks were observed. Only two apparent peaks appeared in the spectrum, one is the monomer dimethoate ion (1.62 cm^2 V^{-1} s^{-1}), another is the dimethoate dimer ion (1.27). The interferences from other constituents could be alleviated largely. The resolution is very good and the response is the strongest for dimethoate in all spectra. Compared to all the above metioned dopants, the effect for the selective detection of dimethoate is the best in mixed acetone−ammonium.
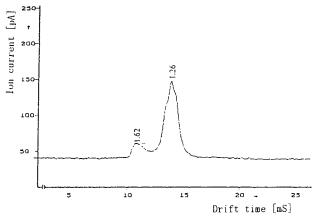
Figure 9. The ion mobility spectrum of dimethoate with acetone and ammonium. (Peak at 1.62 is the acetone dimer ion, 1.54 is the monomer ion, and 1.26 is the dimer ion of dimethoate.)

Among the three mixed dopants, the best selectivity can be obtained in ammonium−acetone which can almost eliminate the interferences from other constituents in dimethoate. The effects of mixed alternate reagent ions are better than the results obtained by using the single solvents. The mixed solvents can not only minimize the appearance of the peaks of those constituents in dimethoate but can also reduce the peak abundance of themselves. However, the principal component takes advantage of acquiring more charges owing to its higher proton affinity. Hence the resolution and the response can be further improved.

3. Relationship between the Concentration of Ammonium and the Response of Dimethoate. The concentration of ammonium added into the carrier gas should affect the response of the analyte. If ammonium cannot occupy all regions of the ion source, the high-concentration solvent in dimethoate can yield its product ion by reacting with the hydrated protons that still exist in the source, and the response intensity of dimthoate will be impaired. On the other hand, ammonium at the excess concentration will also decrease the response of dimethoate owing to the dilution effect and complicated molecule−ion reactions between reagents and the analytes. The addition of ammonium at appropriate concentrations can provide the strongest response of dimethoate. The relationship curve between the concentration of ammonium and the response intensity of dimethoate is depicted in Figure 10. The strongest response of dimethoate was given in ammonium at ~1.0 μg/L.

4. Relationship between the Concentration of Mixed Ammonium−Acetone and the Response of Dimethoate. The same situation existed in the addition of the mixed ammonium−acetone. The curve is described in Figure 11. The concentration of acetone was changed from 0 to 2.0 μg/L while ammonium was kept at 1.0 μg/L. Ammonium at 1.0 μg/L and acetone at ~1.0 μg/L showed the best result.

5. Comparison between the Direct Determination and Selective Determination in a Field Test. The above results were obtained in the laboratory. Additionally, a field test was taken in a row of trees just watered by emulsifiable dimethoate. A portable IMS was directly used to detect the residues of dimethoate in ambient air of the trees. The result is described in Figure 12. The spectrum is similar to that of the headspace
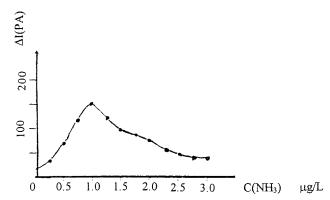

Figure 10. The relationship curve between the concentration of ammonium and the response of dimethoate.
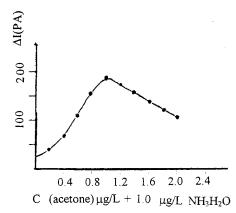

Figure 11. The relationship curve between the concentration of ammonium−acetone and the response of dimethoate.
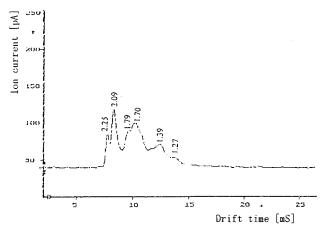

Figure 12. The IMS spectrum of dimethoate in a field test. (Peaks at 2.25 and 2.09 are the reactant ions, 1.79, 1.70, 1.62, 1.48, and 1.39 are the constituents in dimethoate, and 1.27 is the dimer ion of dimethoate.)

vapor shown in Figure 1. Such a complex and broad spectral pattern can hardly provide usable information.

Subsequently, a permeation tube filled with ammonium and acetone was mounted at the sample inlet of the IMS to provide the alternate reagent gases. The hand-held IMS was operated under the identical conditions as before. The spectrum is shown in Figure 13. Almost the peaks of other constituents were alleviated as the results found in the laboratory.

By the comparison between the two methods, a suitable dopant is very useful for the selective detection of dimethoate in field
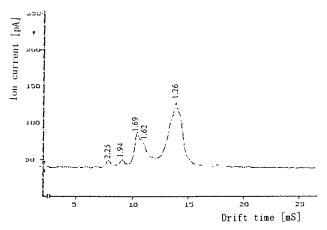
Figure 13. The IMS spectrum of dimethoate with mixed dopants in a field test. (Peaks at 2.25, 1.94 1.69, and 1.62 are the reactant ions, 1.52 is the monomer ion, and 1.26 is the dimer ion of dimethoate.)

tests by simplifying its response. For other complicated samples, the mixed alternate reagent ions method in IMS may supply a way to monitor them.

6. A Model Derived from the Above Results. Assume an analyte has middle proton affinity in a mixed compound, just as with dimethylbenzene in a dimethoate emulsifiable compound. If only one alternate reagent with proton affinity lower than that of the analyte was chosen to improve the selectivity, all peaks of components whose proton affinities are higher than that of the dopant may be observed. The peak of the analyte cannot be determined without the comparison of the standard sample. The use of several dopants having different proton affinities is suggested under such a situation. The method is described as follows:

A, B, and C are three constituents in a mixed sample, B is the analyte, and $P_A(A) < P_A(B) < P_A(C)$. Two suitable dopants D and E are chosen (Their ion mobility spectra are known.) and $P_A(A) < P_A(D) < P_A(B) < P_A(E) < P_A(C)$. When D is added into the carrier gas, the peak of A will be eliminated. There are peaks of D, B, and C in the spectrum. Then the second dopant E is added into the another original sample, peaks of A and B will be eliminated, and only peaks of E and C exist in the spectrum. Since peaks of D and C have been determined, the peak of B can be derived from the former spectra.

For example, if dimethylbenzene is the analyte in our experiment, acetone and ammonium are useful for its detection when the identification methods of IMS-MS and the standard sample addition are absent. Acetone can give the three peaks of dimethylbenzene, the monomer ion, and dimer ion of dimethoate. Ammonium only gives the peaks of dimethoate. The peak of the dimethylbenzene can be obtained.