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Short communication

Determination of interfering triazine degradation products by gas chromatography–ion trap mass spectrometry

Matthew L. Magnuson*, Thomas F. Speth, Catherine A. Kelty

United States Environmental Protection Agency, National Risk Management Research Laboratory, Water Supply and Water Resources Division, Treatment Technology Evaluation Branch, 26 W. Martin Luther King Drive, Cincinnati, OH 45268, USA

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Abstract

Deethylatrazine (DEA), an atrazine degradation product, has been added to the US Environmental Protection Agency's Drinking Water Contaminant Candidate List (CCL). In its gas chromatographic analysis, DEA can coelute with deisopropylatrazine (DIA), another degradation product. The present work demonstrates that the coelution of DEA and DIA can induce a significant (up to ~50%) positive bias in the DEA determination, when using an ion-trap mass spectrometer as the detector. The DIA determination is unaffected by the coelution within experimental error. This may be explained in terms of gas-phase ion fragment populations. A correction factor to the observed DEA concentration may be developed based on the measured DIA concentration. Published by Elsevier Science B.V.

Keywords: Atrazines; Deethylatrazine; Deisopropylatrazine; Triazines; Pesticides

1. Introduction

Triazine compounds are commonly used herbicides in North America. As the potentially adverse health effects of these compounds have become better understood, there has been increased interest in regulating these compounds in drinking water and drinking water sources. Atrazine, a possible human carcinogen, is currently regulated in the United States in drinking water at an action level of 3 μg/l. Because of their structural and toxicological similarity [1], the metabolic degradation products of atrazine, in particular deethylatrazine (DEA), have been added to the US Environmental Protection Agency (EPA)'s Drinking Water Candidate Contaminant List (CCL) [2,3]. This is the list from which future regulated compounds will be selected. To properly study treatment options for DEA, analytical techniques are needed to quantify the contaminant at suitable concentrations.

Mass spectrometry (MS) is often employed for the simultaneous analysis of DEA, an atrazine degradate, and deisopropylatrazine (DIA), a degradation product of atrazine, simazine and cyanazine. Triazine compounds and other herbicides have been determined through the use of liquid chromatography coupled with mass spectrometry [4–6] with detection limits to 0.4 ng/l. Detection limits in the ng/l range are achieved by gas chromatography (GC)–MS [7–9,12] or GC–MS–MS [10,11,13] analysis preceded by a 200–1000-fold preconcentration step involving solid-phase or liquid–liquid extraction.

*Corresponding author. Tel.: +1-513-569-7321; fax: +1-513-569-7658.

E-mail address: magnuson.matthew@epa.gov (M.L. Magnuson)

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As part of recent investigations in this laboratory into the use of activated carbon as a treatment technology to remove DEA, GC–MS was used to quantify DEA. It was observed that the presence of DIA produced a positive interference in DEA quantification, thus resulting in an over-reporting of the DEA value. Occurrence studies [14–16] indicate that concentrations of DIA may be significant in certain source waters and comparable to the DEA concentration. For example, the EPA Pesticide in Groundwater Database [14] indicates the presence of concentrations of DEA up to 2.8 μg/l and DIA up to 3.5 μg/l. Therefore, the interference by DIA on DEA determination was systematically investigated, and the results are summarized in this paper.

2. Experimental

2.1. Reagents

DEA and DIA were obtained from Chem Services (West Chester, PA, USA). Solutions of DEA were not observed to contain DIA by GC–MS, and vice versa. Methyl *tert*.-butyl ether (MTBE), Optima from Fisher was used. To eliminate errors from extraction and preconcentration, MTBE solutions of DEA and DIA were prepared by dilution of the appropriate stock solutions. The masses of DEA and DIA were selected to represent quantities that would be expected to be injected as a result of typical preconcentration procedures [7–13].

2.2. Apparatus

A Varian (Palo Alto, CA, USA) Saturn 2000 ion trap mass spectrometer was used with a Varian 3400 GC oven. A HP 5791A mass-selective detector was used with a HP 5890 GC oven. Splitless injections were auto-injected onto (30 m×0.25 μm, 0.25 μm) DB-5MS (J&W, Folsom, CA, USA) and PTA-5 (Supelco, Bellefonte, PA, USA) columns. For the data shown, the GC temperature was initially 45°C and was ramped at 20°C/min.

3. Results and discussion

3.1. Interference from DIA in the determination of DEA using GC–ion trap MS

DEA and DIA produce many common ions in their mass spectra [7,8]. Therefore, m/z 158 and 187, are used in this study to quantify DIA and DEA, respectively. DEA and DIA coelute on both a DB-5MS column and a PTA-5 column, which has a deactivated phase similar to the DB-5MS. Tailing appears to some extent in published chromatograms for (5%-phenyl)–methylpolysiloxane columns [10,12] and polyethylene glycol (''WAX'') [11], a phase which typically produces good peak shapes for amines. For higher concentrations of DEA and DIA, the vertical scale of the chromatographs can cause the tailing to appear very small. Decreasing the temperature ramp rate from 20°C/min to 4°C/min results in better separation, but decreases sample throughput 2–3-fold. With the slower ramp, coelution still occurs, although peak area overlap decreases from 40% to 10%.

Table 1 compiles slope and error data for the calibration plots (area vs. amount DEA added) for eight amounts of DIA co-injected. The addition of the DIA causes an enhancement in the DEA peak area, so the slopes of the calibration plots increase with increasing DIA concentration. Consider 3000 pg DEA and 6440 pg DIA present in the solution. If the calibration curve with 0 pg DIA added was used, based on the calibration slopes, the measured peak area would correspond to 4300 pg of DEA. This is

Table 1
Slope, error and correlation coefficients for calibration curves of DEA prepared with various amounts of deisopropylatrazine (DIA)[a]

DIA injected (pg)	Slope	R^2
0	0.0090±0.0004	0.98
80	0.0092±0.0005	0.98
160	0.0092±0.0004	0.99
402	0.0095±0.0005	0.98
805	0.0098±0.0004	0.99
1610	0.0106±0.0004	0.99
3220	0.0113±0.0002	0.99
6440	0.0121±0.0002	0.99

[a] The curves were fit to a linear equation.

about a 34% overestimation of the amount of DEA. Note that 3000 pg injected corresponds to a 1.5 μg/l solution subjected to a 1000-fold preconcentration with a 2 μl injection. This situation is likely, given recent preconcentration methodology [7–13] and the concentration of DIA and DEA present in some water sources [14–16].

Calibration plots of DIA between 0 and 6440 pg of DIA were prepared for six different DEA amounts between 0 and 5760 pg. The correlation coefficients, generally >0.99, indicate linearity. The slopes for all concentrations are similar within the standard error, indicating that the determination of DIA is essentially independent of the quantity of DEA injected.

3.2. Source of the interference

DEA solutions quantified with a quadrupole instrument (HP 5971A mass-selective detector) were not affected by the presence of DIA. Because the ions in an ion trap mass spectrometer are confined to a limited region of space for a period of time, chemical reactions/interactions are sometimes reported in ion-trap mass spectrometers [17]. Insight into a possible cause for the interference by DIA on DEA determination might be gained through consideration of the fragmentation behavior of DEA and DIA. Fig. 1 shows possible fragmentation pathways for DEA and DIA. Because DEA and DIA are structurally similar, the fragmentation of both DEA and DIA produces an ion with m/z 172 through different mechanisms. The presence of additional amounts of this common ion from DIA may shift the gas phase ion reaction toward m/z 187 for DEA, effectively enhancing its signal, corresponding to the experimental observation. By contrast, there is no common fragment with m/z 158. Thus, the signal from DIA is not affected, while DIA may enhance the DEA signal via the equivalent, common ion. A detailed analysis of the kinetics and thermodynamics of these reactions is beyond the scope of this paper.

3.3. Strategies for quantifying DEA in the presence of DIA

The interference can either be avoided or corrected for. Most GC columns are expected to result in this interference to some degree, depending on the temperature program and the column's age. One way to reduce the interference is to allow a slow temperature ramp. The disadvantage of using a slower temperature program is that productivity drops,

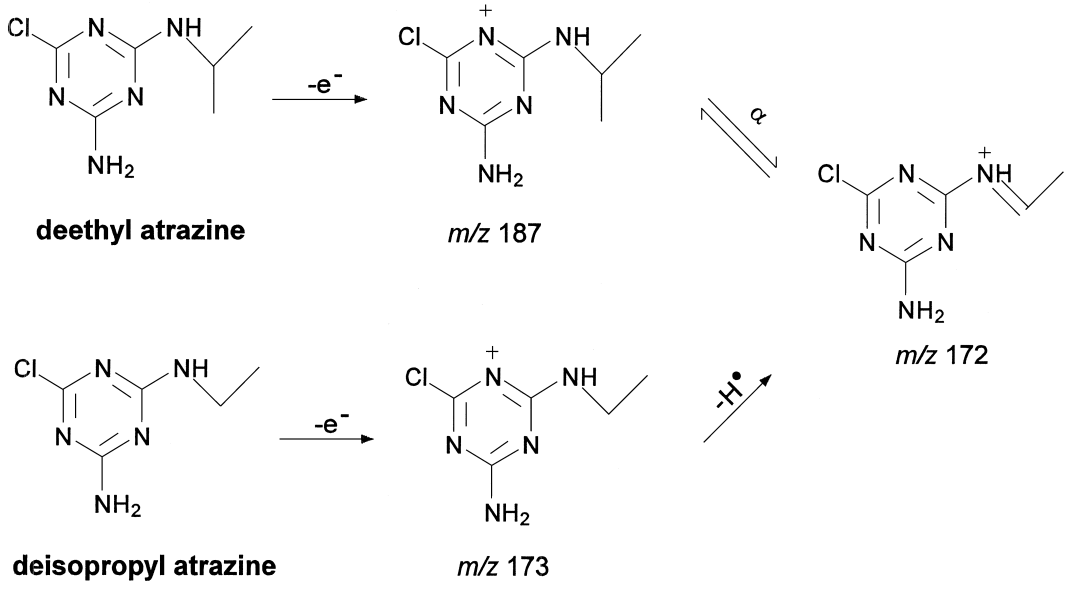

Fig. 1. Gas phase reaction pathways for DEA and DIA.

perhaps unacceptably. However, even for a slower temperature ramp, the peaks may coelute as the column ages, negating the benefits of the slower ramp. Changing the operational parameters of the trap, namely the ionization time and ion target level, were investigated as a means of mitigating the interference. Both of these approaches were unsuccessful in terms of maintaining adequate sensitivity and were not pursued. Another avoidance strategy is to use a quadrupole instrument, for which this interference does not appear. However, ion trap instruments can provide sensitivity and be relatively inexpensive, so they are used for herbicide analysis in many research [7,10,11,13] and production laboratories.

For laboratories which require high productivity and have ion trap mass spectrometers in use, a practical solution is to apply a correction based on the DIA concentration. To do this, a plot similar to Fig. 2 may be constructed. Fig. 2 is the correction to the DEA concentration versus the amount of DIA measured in solution. The correction is calculated as the ratio of the slopes of the calibration curves in Table 1. The correction factor at any DIA concentration can be calculated from the best fit line in Fig. 2, a second-order polynomial. Thus, to calculate the actual DEA concentration, the apparent DEA concentration, determined from the calibration plot with zero added DIA, is multiplied by the correction factor (Fig. 2) calculated from the amount of DIA present. As the column ages, this correction factor may change and should be accounted for. The data in the graph were obtained using a new PTA-5 column. On an aged DB5-MS column placed into the same instrument, the peaks coelute more, and a 46% error was calculated, versus 34% for the new column for the calibration plot with 6440 pg DIA.

4. Conclusion

It has been demonstrated that DIA interferes with the determination of DEA for GC–MS determination with an ion trap mass spectrometer. Strategies for determining DEA in the presence of DIA are presented. Because the interference may result from gas

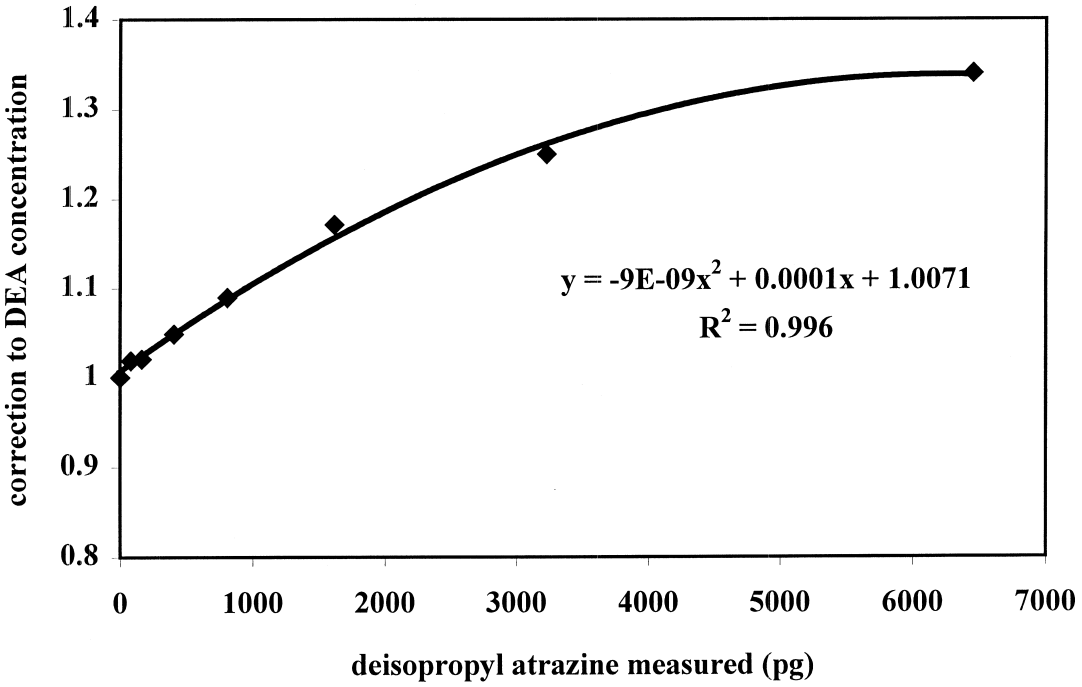

Fig. 2. The correction factor for the apparent DEA concentration as a function of the quantity of DIA measured.

phase ion chemistry within the ion trap, it also may affect MS–MS determinations performed with ion trap instruments [10,11,13]. It is straightforward to apply a correction factor based on the amount of DIA determined to accurately evaluate DEA. The use of the correction factor allows faster temperature ramps to be used and also may help extend the useful lifetime of the column.

5. Notice

Use of trade names or specific manufacturers equipment or supplies does not constitute endorsement by US EPA.

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