A Rapid Technique for the Confirmation of Iodine and Red Phosphorus Using Direct Analysis in Real Time and Accurate Mass Spectrometry

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ABSTRACT: Iodine and red phosphorus are chemicals commonly seen in clandestine methamphetamine laboratories. Current analytical methods used for the confirmation of these chemicals include FTIR and GC/MS, usually after a derivatization or reaction with other compounds. X-ray diffraction and scanning electron microscope-energy dispersive x-ray analysis are also used to confirm these chemicals, but all of these techniques tend to be time-consuming or produce poisonous products. A novel technique, using the JEOL-IonSense AccuTOF-DART™ system, has been developed which yields accurate mass spectra usually in less than ten minutes of analysis time, with no sample preparation.

KEYWORDS: iodine, red phosphorus, Direct Analysis in Real Time, mass spectrometry, clandestine laboratory, methamphetamine, forensic chemistry

The prevalence of clandestine methamphetamine laboratories poses analytical challenges for forensic laboratories to identify the chemicals used in the clandestine process. Two of these chemicals, iodine and red phosphorus, are encountered in the syntheses involving the reduction of ephedrine or pseudoephedrine to methamphetamine via hydriodic acid [1]. If these chemicals are found at a clandestine laboratory site, their chemical identification becomes crucial in demonstrating their role in the manufacture of methamphetamine for prosecution in court.

Several presumptive screening tests and qualitative methods are currently employed to identify iodine and red phosphorus [2]. These methods typically involve conversion of the iodine or red phosphorus to other compounds, such as hydriodic acid or white phosphorus, the handling of which may be hazardous due to the nature of these new derivatives. The derivatives are then identified via FTIR or GC/MS. X-ray diffraction and scanning electron microscopy with energy dispersive spectroscopic analysis may also be used to identify iodine and red phosphorus [3-5].

The Direct Analysis in Real Time (DART™) (Ion Sense, Saugus, MA) source is beginning to see widespread use in forensic work [6-10]. A detailed description of the theory and operation of the DART source is given by Cody, *et al.* [11,12]. Other applications of DART span the entire field of chemistry [13-52]. In this work, the DART ion source was coupled with an accurate mass time of flight mass spectrometer (AccuTOF™ JEOL, Inc., Peabody, MA) to determine the elemental composition of solid samples held in a heated gas stream. No sample preparation was needed for the analysis of iodine and red phosphorus, and the analysis of each took less than ten minutes to complete.

Experimental

Iodine and red phosphorus were obtained from Mallinckrodt, (St. Louis, MO).

Experiments were carried out using the DART ion source coupled to a JEOL AccuTOF mass spectrometer (JMS-100LC) operated in positive-ion mode. This system was controlled by "Mass Center" software (JEOL, Inc.). The AccuTOF was tuned by infusion of reserpine (Sigma-Aldrich, Inc.) through an electrospray ion source to meet the manufacturer's recommendations for resolution (>6000). These tune settings were then utilized for all AccuTOF-DART analyses. Daily calibration was checked by sampling a methanol (Fisher Scientific, Fair Lawn, NJ) solution of methyl stearate (Eastman Kodak, Rochester, NY) (2 mg/mL). In order to pass daily calibration, the measured mass of the $[M+H]^+$ of methyl stearate was required to be within $\pm$ 3.0 mDa of the calculated mass for this ion (299.2950 Da).

For the iodine analysis, the measurements were taken with the ion guide peak voltage at 600 V, reflectron voltage at 910 V, orifice 1 voltage at 20 V, orifice 2 voltage at 5 V, ring lens voltage at 6 V, and an orifice 1 temperature of 80°C. The mass range was 66-600 Da. The DART ion source was used with the helium gas flow rate at 2.5 L/min, gas heater temperature of 275°C, discharge electrode needle at 4000 V, electrode 1 at 150 V, and electrode 2 at 250 V. Internal mass calibration was achieved using a dilute solution of polyethylene glycol (PEG) 600 (Chem. Service, West Chester, PA) in methanol sampled within each data file. After sampling the PEG solution, a crystal of solid iodine was held in the DART gas stream using tweezers until it sublimed. No other sample preparation was performed.

For the red phosphorus analysis, the measurements were taken with the ion guide peak voltage at 100 V, reflectron voltage at 910 V, orifice 1 voltage at 200 V, orifice 2 voltage at 10 V, ring lens voltage at 15 V, and an orifice 1 temperature of 80°C. The mass range was 38-100 Da. The DART ion source was used with the helium gas flow rate at 2.5 L/min, gas heater temperature of 350°C, discharge electrode needle at 4000 V, electrode 1 at 150 V, and electrode 2 at 250 V. Internal mass calibration was achieved using the protonated molecule of acetone (EM Science, Gibbstown, NJ) at 59.0497 Da as a drift compensation lock mass. A clean glass melting point tube (Kimble Glass, Vineland, NJ) was dipped into the liquid

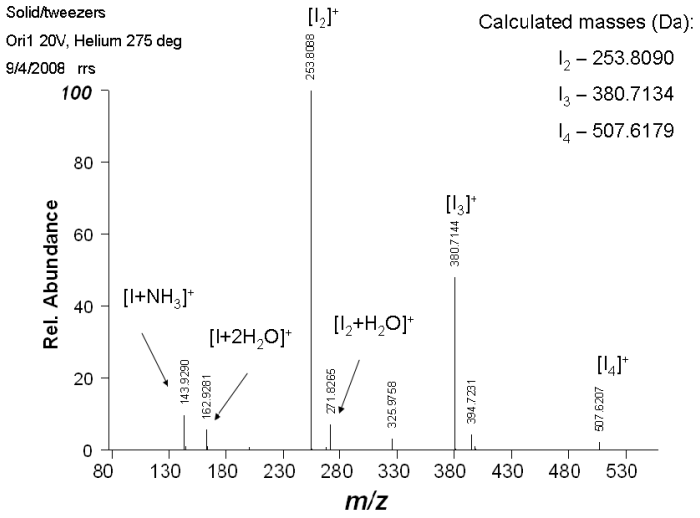

Figure 1 - AccuTOF-DART mass spectrum of iodine.

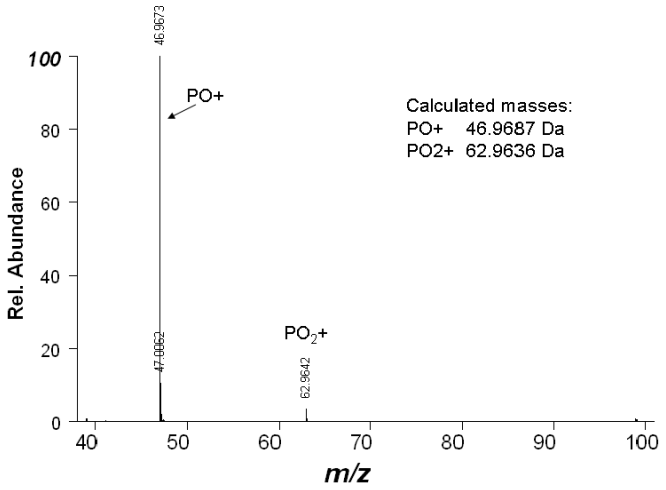

Figure 2 - AccuTOF-DART mass spectrum of red phosphorus.

acetone and held in the DART gas stream to produce an accurate mass spectrum. Another melting point tube was then dipped into the red phosphorus and a very small amount of red phosphorus clung to the glass tube. This sample was then held in the DART gas stream. No other sample preparation was performed.

Calculated masses were determined using empirical formulas and IsoCalc version 4.1, part of Mass Spec Tools, published by ChemSW, Inc. (Fairfield, CA).

Results and Discussion

Figure 1 shows the AccuTOF-DART mass spectrum of solid iodine. The major ion at 253.8088 Da is from the diatomic molecule of iodine $[I_2]^+$, which has a calculated mass of 253.8090 Da. Other ions seen in the spectrum include $[I_3]^+$ at 380.7144 Da (calculated mass 380.7134 Da), $[I_4]^+$ at 507.6207 Da (calculated mass 507.6179 Da), $[I+NH_3]^+$ at 143.9290 Da (calculated mass 143.9310 Da), $[I+2H_2O]^+$ at 162.9281 Da (calculated mass 162.9256 Da) and $[I_2+H_2O]^+$ at 271.8265 Da (calculated mass 271.8195 Da). These are all highly characteristic ions resulting from the sublimation of iodine in the heated gas stream. Addition product ions with water and ammonia were from the atmosphere around the instrument.

Figure 2 shows the AccuTOF-DART mass spectrum of red phosphorus. The measured ions at 46.9673 Da and 62.9642 Da represent $[P+O]^+$ and $[P+O_2]^+$, respectively. The calculated masses for these ions are 46.9687 Da and 62.9636 Da. It is important to note that there are no other combinations of atoms that will give peaks at these masses.

The AccuTOF-DART analysis of iodine and red phosphorus is an extremely rapid technique that can easily be included in the forensic identification scheme for these common chemicals, with no sample preparation required.

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