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Ambient Mass Spectrometric Detection of Organometallic Compounds Using Direct Analysis in Real Time

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The present work describes the mass spectrometric detection of organometallic compounds following their atmospheric pressure ionization using a commercial direct analysis in real time (DART) ion source. Several organometallic compounds of As, Fe, Hg, Pb, Se, and Sn were examined, and their corresponding mass spectra as well as induced fragmentation patterns were recorded. Gas phase sampling of the pure organometallic compounds or their solutions prepared in toluene generated temporally stable signals. For the majority of the compounds, the molecular ion or protonated molecule was detected; noticeable exceptions are the tetra-substituted compounds for which their less-substituted species dominated. The organometallic species were used as model compounds for a systematic investigation of the impact of operating parameters of the DART source, including gas temperature and electrode voltages. In general, results have shown that powering the electrodes designed to remove ions from the DART gas stream results in a reduction in signal intensity for most of the compounds investigated, suggesting that charged species from the plasma play an important role in the ionization process of the test analytes.

The allure of undertaking qualitative and quantitative characterization of analytes in real time under ambient atmospheric conditions is appealing, all the more so as liquids, solids, and gases can be directly interrogated with little or no sample preparation.[1] Desorption electrospray ionization mass spectrometry (DESI),[2] desorption atmospheric pressure chemical ionization (DAPCI),[3] direct analysis in real time (DART),[4] electrospray-assisted laser desorption/ionization (ELDI),[5] atmospheric solids analysis probe (ASAP),[6] matrix assisted laser desorption electrospray ionization (MALDESI)[7] and flowing atmospheric pressure afterglow (FAPA)[8] desorption/ionization techniques, among others, have been described as ambient mass spectrometry techniques. Target molecules are typically volatile and semivolatile compounds present on various substrates or incorporated into biological tissues, polymeric materials, pharmaceutical formulations, natural products, and forensic samples, including agrochemicals, drugs, explosives, proteins, and metabolites with detection power extending into the picogram range.[9] Ambient-MS imaging at submillimeter resolution has also been reported.[10]

To date, the application of ambient MS techniques to the detection and identification of organometallic compounds, particularly those that may be of environmental and/or toxicological importance, has not been extensively addressed. In a brief applications note from JEOL Inc., several characteristic mass spectra of solid particles of iron, tungsten, rhodium, and platinum compounds were generated by DART.[11] Also, Nath et al. employed DART for the characterization of diorganotin (IV) complexes of tetraazamacrocyclic ligands.[12] Anthropogenic and naturally occurring organometallic compounds are significant from the viewpoint of fundamental speciation, environmental geochemical cycling, and metabolism and toxicology.[13] As one of the principal encumbrances facing speciation is the preservation of the chemical form of the analyte when significant sample manipulation is required prior to detection. Under such circumstances, the

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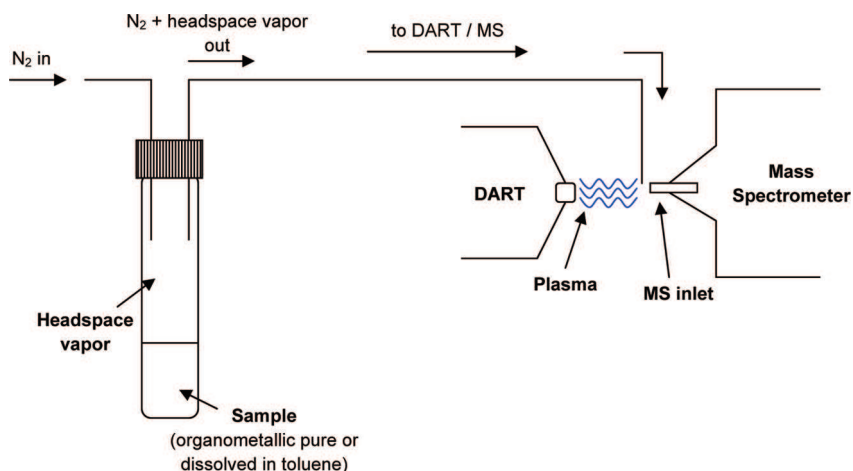
Figure 1. Schematic representation of the setup for gas phase sampling of organometallic compounds for detection by DART-MS.

attractive direct analysis feature offered by ambient MS techniques is clear. This study was undertaken to assess the potential of DART for detection of a range of volatile and semivolatile small molecule organometallic species and the impact of operating parameters on response. For this purpose, several organometallic compounds of As, Fe, Hg, Pb, Se, and Sn were examined.

EXPERIMENTAL SECTION

Instrumentation. *Mass Spectrometry.* Detection was performed on an LTQ mass spectrometer (Thermo Fisher Scientific Inc., Bremen, Germany) equipped with an electrospray ion source. Full scan m/z 60−450 using linear ion trap was acquired in either positive or negative ion mode. The capillary temperature was set at 250 °C. The tube lens voltage was set to 95 V, and capillary voltage was set to 39 V. For MS/MS experiments, an isolation width of 1.2 amu was used.

DART. The DART (Ionsense, Saugus MA) ion source was mounted to the mass spectrometer as recommended by the manufacturer after removing the existing electrospray source. The orifice of the DART ion source was positioned such that the stream of helium or nitrogen exiting the source was in line with the inlet orifice of the mass spectrometer. The distance between the outlet of the DART ion source and the inlet orifice was approximately 17 mm. (This distance was fixed due to physical constraints presented by geometry of the DART ion source and the mass spectrometer.)

Sample Introduction Apparatus. Gas phase sampling of organometallic compounds was achieved as schematically shown in Figure 1. The pure compounds or their respective 1.0 g L^{-1} solutions in methanol or toluene (nominally 2 mL) were placed into 5 mL screw-capped glass vials which were then sealed with silicone septa. Nitrogen was used as a purge gas at flow rates between 85 and 400 mL min^{-1}. Headspace vapors were directed by the N$_2$ flow toward the inlet of the mass spectrometer via a 30 cm 1/16 in ID Teflon transfer line held at room temperature and positioned in front of the exit nozzle of the DART source. The glass vial could be optionally heated using a wrap of resistive heating tape to a temperature of up to ca. 80 °C. An alternative approach to direct sampling was accomplished by manually positioning a cotton tipped applicator (Q-tip, Calapro, Yorba Linda CA) in front of the inlet of the mass spectrometer onto which a nominal 0.2 mL volume of sample had been

absorbed, so as to directly expose it to the plasma stream from the DART source.

Safety Precautions. The studied organometallic compounds are highly toxic. Use of adequate ventilation/fume extraction and PPE are necessary.

RESULTS AND DISCUSSION

Mass spectra of a number of volatile and semivolatile organometallic compounds of interest were acquired using DART MS. The analyte was presented to the ionization source either in gaseous form, following transfer of the vapor in a stream of N$_2$ from the pure compound or a prepared solvent medium, or by sampling of a solution of the compound from an absorbent surface.

Vapor Phase Sampling. *Arsenic and Selenium Compounds.* DART mass spectra were obtained from gas phase sampling of pure triethylarsine [TEA; (CH$_3$CH$_2$)$_3$As] and diphenylselenide [DPS; (C$_6$H$_5$)$_2$Se]. Triethylarsine could be readily detected using both He and N$_2$ plasma gases. Use of He resulted mainly in the formation of the protonated molecule, [M + H]$^+$, at m/z 163 and the O + H adduct at m/z 179, whereas a N$_2$ discharge gas favors formation of a series of larger mass products (m/z 300−600), most likely oligomers of TEA, in addition to the protonated molecule, which could also be detected but with lower signal intensity compared to ionization in He.

Gas phase sampling of pure DPS resulted in a signal at m/z 157 corresponding to [C$_6$H$_5$Se]$^+$ when He was used as the discharge gas. Higher-intensity signals, and additional product ions such as that at m/z 251 (base peak; [C$_{12}$H$_{10}$Se + NH$_3$]$^+$) or [C$_{12}$H$_{10}$Se + O + H] and the molecular ion itself at m/z 234, were detected when N$_2$ was used. Again, the use of a N$_2$ plasma proved less efficient at inducing fragmentation and, in the specific case of DPS, higher intensity signals could be generated. The higher internal energy of helium coupled with its higher thermal conductivity could account for the enhanced fragmentation observed with this gas as compared to nitrogen.

Iron, Lead, and Mercury Compounds. Detection of *N,N*-dimethylaminomethyl ferrocene (DMAMF, C$_{13}$H$_{17}$FeN) with gas phase sampling was successful using both He and N$_2$ as the plasma gas for the DART source. Although the net intensity of the protonated molecule ([M + H]$^+$) at m/z 244 was similar in either gas, the intensity of the methylated ferrocene deriva-
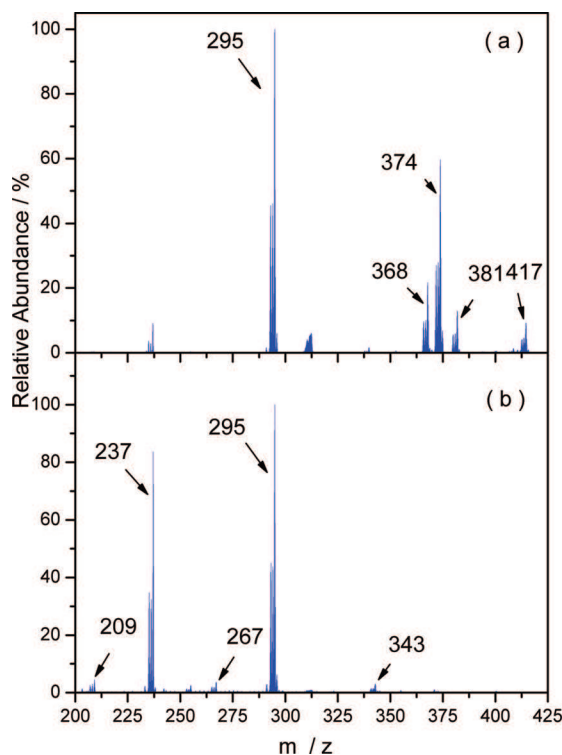
Figure 2. Positive ion spectra obtained with DART by gas phase sampling of pure tetraethyllead: (a) with N_2 plasma, low flow rate (1.0 L min^{-1}); (b) with He plasma (6.0 L min^{-1}). The mass spectra show prominent peaks at m/z 209 (protonated lead ion), 237 [C_2H_5Pb]$^+$, 267 [$(C_2H_5)_2Pb + H$]$^+$, 295 [$(C_2H_5)_3Pb$]$^+$, 343 [$M + H_2O + H$]$^+$ and solvent adducts of the TEL at m/z 368, 374, 381, and 417.

tive at m/z 199 (base peak; $(C_5H_5)(C_5H_4)CH_2Fe^+$, likely a fragment derived from the DMAMF) was at least an order of magnitude higher with He compared to the signal obtained in N_2.

Detection of vapor species derived from solid trimethyllead chloride [TML; $(CH_3)_3PbCl$] could only be accomplished using He as the plasma gas, and only the trimethyllead moiety [$(CH_3)_3Pb$]$^+$ at m/z 253 and methyllead [CH_3Pb]$^+$ at m/z 223 were evident. Despite the fact that TML chloride was used for all measurements, no chloride-containing species could be detected in the vapor phase in either positive or negative ion mode.

Response from tetraethyllead (TEL) using a He plasma was considerably higher than in N_2; otherwise, spectral differences were negligible. The only noticeable exception was that use of very low flow rates of N_2 (below 2 L min^{-1}) resulted in formation of a series of lead containing peaks at m/z 368, 374, 381, and 417, which could be solvent adducts of the TEL, as identified in Figure 2a. Dealkylated fragments and the protonated lead ion were also detected, as identified in Figure 2b.

Gas phase sampling of solid methylmercury chloride (MeHgCl) resulted in spectra with the characteristic ion at m/z 217 (CH_3Hg^+) using either He or N_2 as the plasma gas, although higher-intensity was obtained using He. A peak at m/z 235 was also detected, corresponding to [$MeHg + H_2O$]$^+$. The characteristics of dilute solutions (about 1.0 g L^{-1}) of MeHgCl prepared in organic solvents were also evaluated using gas phase sampling. The first approach, using dilution in methanol, did not provide detectable peaks with the characteristic isotope
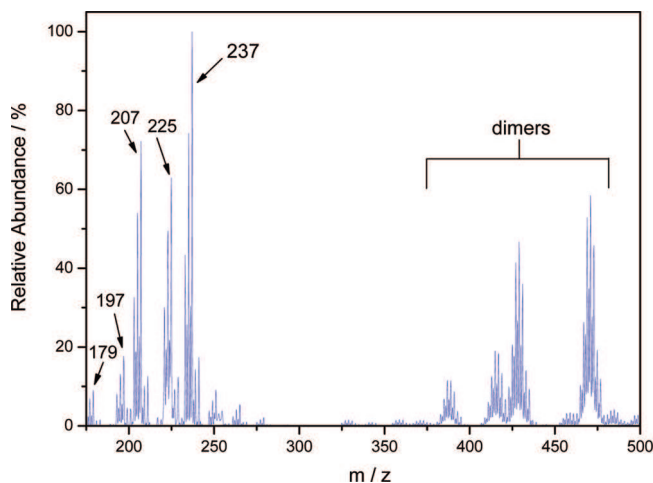

Figure 3. Positive ion spectra generated in He plasma (6.0 L min^{-1}) with DART by gas phase sampling of pure tetraethyltin. Prominent peaks at m/z 179 [$(C_2H_5)_2Sn + H$]$^+$, 197 [$(C_2H_5)_2Sn + H_2O + H$]$^+$, 207 [$(C_2H_5)_3Sn$]$^+$, 225 [$(C_2H_5)_3Sn + H_2O$]$^+$, and 237 [$M + H$]$^+$ are evident.

pattern of Hg, even after heating the solution to near boiling. Dissociation of the mercury salt in the solution and/or significant dilution of the analyte in the headspace due to the high vapor pressure of methanol may account for this. Consequently, a lower-polarity and relatively less volatile solvent was selected to conduct further experiments. A 1.0 g L^{-1} solution of MeHgCl in toluene resulted in a single peak at m/z 309, corresponding to a toluene-solvated MeHg ion. Similar experiments aiming at detection of ethylmercury chloride (EtHgCl) from either the pure compound or methanolic solutions were unsuccessful.

Organotin Compounds. *Methyl-, Ethyl-, and* n-*Propyltin Compounds.* Gas phase sampling of pure tetramethyltin chloride (TMT) using a He plasma typically provided peaks identified as hydrated trimethyltin ion ([$(CH_3)_3Sn + H_2O$]$^+$; base peak at m/z 183), trimethyltin ion ([$(CH_3)_3Sn$]$^+$; m/z 165), and to a dimer, with methyl loss at m/z 345. The use of a N_2 plasma shifted the base peak to the protonated dimer at m/z 347.

Gas phase sampling of tetraethyltin (TET) using He as the DART gas resulted in a number of tin containing peaks as shown in Figure 3. The base peak at m/z 237 corresponds to the protonated molecule ([$M + H$]$^+$); dealkylated fragments are also evident in Figure 3, along with a series of dimers with m/z between 329 and 485. When low He flow rates were used, the base peak was the TET dimer at m/z 471. The use of a N_2 plasma enhanced the intensities of dimeric species perhaps for reasons discussed above with respect to diphenylselenide.

A 1.0 g L^{-1} solution of tri-n-propyltin chloride (TPT) in toluene provided the tripropyltin ion ([$(C_3H_7)_3Sn$]$^+$) with m/z 249 as the base peak in a He plasma. Other high-intensity peaks at m/z 267 corresponding to the hydrated TPT ion ([$M + H_2O$]$^+$) and at m/z 309 were also detected. The N_2 plasma also produced ions at m/z 249 (TPT) and 349 with a base peak at m/z 357, which could be due to a highly substituted hydrated propyltin compound.

Tetrapropyltin (TetraPT) was readily detected by gas phase sampling of the pure liquid. A helium plasma gas produced higher intensity signals compared to N_2. The base peak was detected
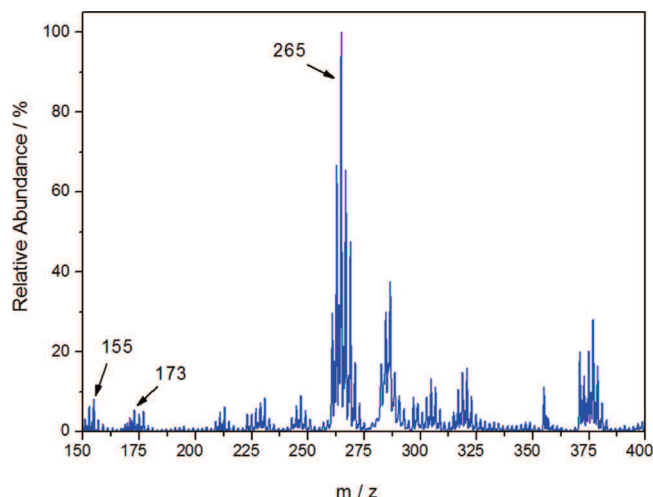
Figure 4. Positive ion spectra generated in He (6.0 L min^{-1}) plasma with DART by gas phase sampling of pure mono-n-butyltin. Peaks at m/z 155, 173, and 265 correspond to [SnCl]$^+$, [SnCl + H$_2$O]$^+$, and [MBT + 2Cl + H$_2$O]$^+$, respectively.

at m/z 225, corresponding to the hydrated protonated dipropyltin ion, [(C$_3$H$_7$)$_2$Sn + H$_3$O]$^+$. A signal at m/z 445 with a complex dimer-like isotope pattern could also be detected, and the peak intensity at this specific m/z was found to be particularly intense when N$_2$ was used as the plasma gas. Several other peaks corresponding to less substituted Sn compounds were also detected, ranging from m/z 150 to 225. Toluene solutions of TetraPT (1.0 g L^{-1}) were also investigated using gas phase sampling. Two pronounced peaks at m/z 249 (TPT$^+$) and 267 ([TPT + H$_2$O]$^+$) were generated.

n-*Butyltin Compounds.* The mass spectrum of pure monobutyltin trichloride (MBT) is shown in Figure 4. Several peaks corresponding to tin chloride species could be identified, including the hydrated MBT dichloride ion, [Sn(C$_4$H$_9$)Cl$_2$ + H$_2$O]$^+$ at m/z 265.

Attempts to examine dilute solutions (1.0 g L^{-1}) of MBT utilizing methanol or acetone as the solvent were not successful. Only from toluene solutions (negative ion mode) were tin species detected at m/z 225, 241, and 258, likely various tin chlorides, but no signal for alkylated tin species (butyltin) could be detected.

Neither gas phase sampling of pure solid dibutyltin chloride (DBT) nor solution based sampling from a methanolic solution yielded signals. In negative ion mode, various tin chloride species could be detected from toluene solution but no DBT.

The spectrum obtained by gas phase sampling of pure tri-n-butyltin (TBT) contained solely the tributyltin ion [(C$_4$H$_9$)$_3$Sn]$^+$, at m/z 291. Signals were only generated using a N$_2$ plasma and with relatively low intensity. When dissolved in toluene (1.0 g L^{-1} solution), the He plasma produced signals with intensities an order of magnitude higher than those with N$_2$, mainly at m/z 291 (TBT). Low-intensity peaks containing tin were also detected at m/z 399 and 412.

Gas phase sampling of pure tetra-n-butyltin (TetraBT) did not generate any detectable signal. As a 1.0 g L^{-1} solution in toluene, however, a characteristic signal at m/z 291 arises, which corresponds to tributyltin ion. A very low intensity tin containing peak at m/z 399 was also observed. Similar to the situation

arising with gas phase sampling of TetraPT, the molecular ion of the tetra-substituted species was not detected, and the base peak corresponded to the triply substituted ion. As signals for the molecular ions of TMT and TET have been successfully detected, it seems that a steric effect, resulting from bonding with four relatively large-chain radicals, reduces the gas phase stability of TetraPT and TetraBT, and the loss of one alkyl functionality occurs immediately on interaction with the reactive gas phase species from, or generated by, the plasma source.

Solution Sampling. Mass spectra for the entire suite of selected organometallic compounds were successfully generated when 1.0 g L^{-1} solutions prepared in either toluene or methanol were used in a "direct sampling" approach. In this case, Q-tips saturated (0.2 mL) with the corresponding solution were directly exposed to the gas stream from the DART source and real-time spectra generated. Several characteristic peaks for all the studied compounds were detected, with only minor or no changes when compared to the main peaks obtained using gas phase sampling. Direct exposure obviously compromises temporal stability of the spectra, which is due to the rapid vaporization of the organic solution from the absorbent surface, but it has proved to be a consistent means of detecting organometallic compounds, suggesting it may be particularly attractive as a screening procedure.

Evaluation of DART Source Operating Parameters. As gas phase sampling of organometallic compounds generated steady-state signals, an evaluation of the effect of the operating parameters of the DART source could be undertaken. A 5 min integration of the signal intensity obtained for the molecular ion or for the base peak for each organometallic compound was selected. In order to determine whether the operating parameters affected individual gaseous species or resulted in a general effect for all vaporized species, the total ion current (TIC) was simultaneously monitored during all steps of the investigation. It was noted that the TIC is subject to approximately the same effects as those noted for individual ions when altering source operating parameters, indicating that differences in the ionization characteristics of individual compounds are masked by significant changes that occur in the gas stream composition or its physical properties.

Effect of Gas Flow Rate. The influence of plasma gas flow rate on response is illustrated in Figure 5. As can be seen, maximum intensity for most compounds was obtained with flow rates ranging between 2.5 and 3.5 L min^{-1} N$_2$ (Figure 5a). The intensity obtained for the TMT-derived dimer was found to be higher at lower flow rates when compared to those for the molecular ion. A generalization, however, does not seem to be applicable in this case, as maximum intensities for both the dimer and molecular ion of TetET were obtained at the same gas flow rate (3.5 L min^{-1}).

The three organometallic compounds examined using a He plasma have shown similar characteristics in relation to variation of the plasma gas flow rate, as summarized in Figure 5b. Helium flow rates below 6.5 L min^{-1} are less efficient. It is possible that varying the plasma gas flow may also affect ambient temperature and transport as well as analyte and mass spectrometer sampling efficiencies.

Effect of Gas Temperature. The influence of the nominal gas temperature on signal intensity for the series of organometallic
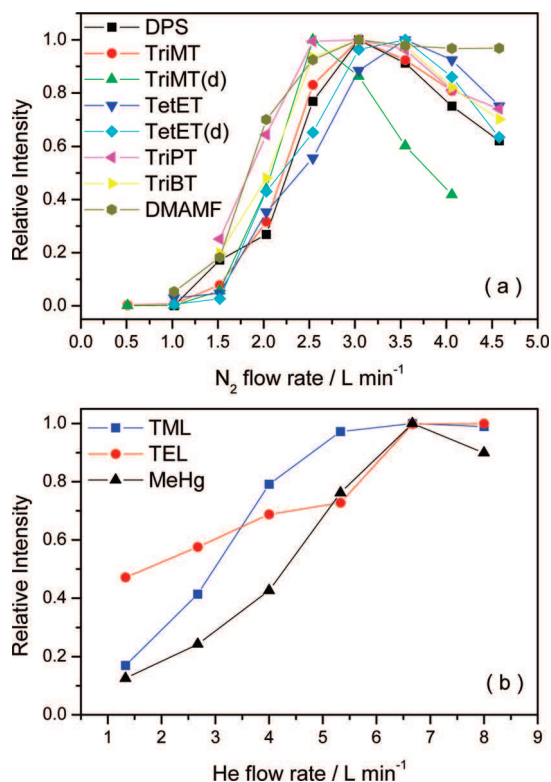
Figure 5. Effect of plasma gas flow rate from the DART source on signal intensity for a series of organometallic compounds employing gas phase sampling: (a) N_2 plasma; (b) He plasma. "d" denotes a dimer species. Conditions: nominal gas temperature 250 °C; discharge electrode 4000 V; secondary and grid electrodes off.

Figure 6. Effect of gas temperature in the DART source on signal intensity for a series of organometallic compounds: (a) Fe, Hg, Pb, and Se compounds; (b) Sn compounds. "d" denotes a dimer species. Helium discharge used for TML, TEL, and MeHg (7.0 L min^{-1}); N_2 discharge (3.0 L min^{-1}) used for the remaining compounds. Conditions: discharge electrode 4000 V; secondary and grid electrodes off.

compounds is shown in Figure 6. A considerably diverse effect of temperature on response for different species is evident, with individual maximum intensities occurring over temperatures ranging from 100 to 300 °C.

Interestingly, for the highly volatile compounds, no heating was necessary for detection (see TML or TetET), suggesting that the primary role of heating the DART discharge gas may simply be to produce gas phase analyte species through thermal desorption for subsequent ionization/dissociation of gas phase clusters.

Effect of Discharge Voltage. The discharge electrode sustains the plasma. An evaluation of the effect of the discharge electrode voltage on signal intensities has shown that they increase linearly with an increase in the electrode voltage, irrespective of the plasma gas used. It remains to be determined whether this is a consequence of an increase in the number of ions, electrons, and metastable species in the gas stream or an increase in their energy in response to the increase in the electrode voltage. Other effects, such as increased temperature of the plasma stream, may exert influence as well, thereby increasing the degree of ionization. A discharge electrode voltage of 4000 V was adopted for all experiments.

Effect of Secondary (Disk) Electrode. The perforated disk (secondary) electrode follows the discharge needle in the DART source chamber and is utilized to eliminate ions from the gas stream.[4] The effect of the secondary electrode voltage on relative signal intensities for the series of organometallic compounds is presented in Figure 7, showing a negligible effect on the relative signal intensity for all compounds in the range −300 to 0 V. At positive voltages, however, a decrease in signal intensity is
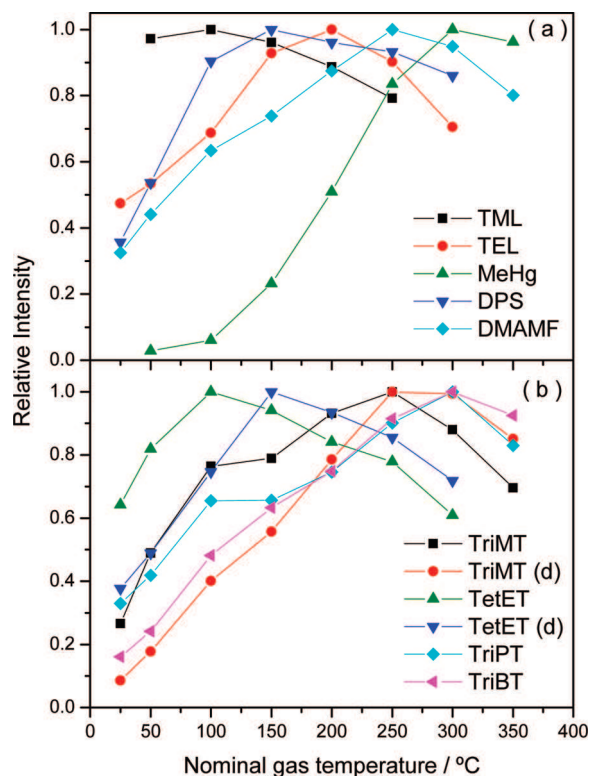
observed for all compounds except when ionization is accomplished using a He plasma (TML, TEL, and MeHg). On the basis of this, it appears that negatively charged species in the gas stream might play an important role in the ionization process, as the apparent removal of these plasma species results in a decrease in signal intensity by up to 50% for some of the organometallic compounds. The apparent inertness of species ionized by the He plasma to changes in the electrode voltage from −300 V to +300 V may be due to the different composition of the plasma compared to that when N_2 is used. It remains unclear, however, if this effect is due to the absence of negatively charged species at appreciable concentrations in the He plasma or if it is a characteristic inherent to the ionization mechanism(s) of TML, TEL, and MeHg.

Effect of Grid Electrode Voltage. A grid electrode located next to the exit nozzle in the DART source is used to minimize ion−ion recombination reactions at the exit of the plasma stream. This often has a significant effect on the elimination of atmospheric reagent ions, such as NO^+, and in reducing "chemical background".

The effect of grid electrode voltage on relative signal intensities for a series of organometallic compounds is shown in Figure 8, wherein it can be seen that signal intensity decreases following application of any (positive or negative) potential to the grid electrode, with the exception of TML for negative voltages. This might suggest participation of species other than neutrals (metastable atoms) in the ionization of gas phase compounds, as the
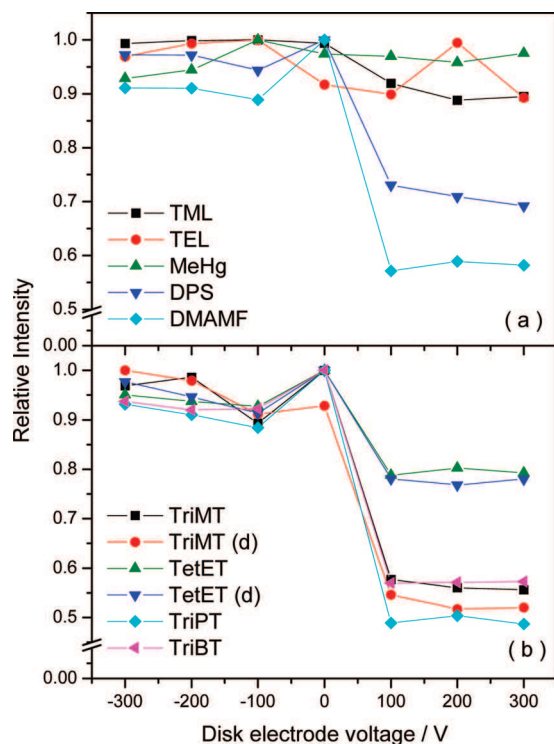
Figure 7. Effect of disk (secondary) electrode voltage in the DART source on signal intensity for a series of organometallic compounds: (a) Fe, Hg, Pb, and Se compounds; (b) Sn compounds. "d" denotes a dimer species. Helium discharge used for TML, TEL, and MeHg (7.0 L min^{-1}); N$_2$ discharge (3.0 L min^{-1}) used for the remaining compounds. Conditions: gas temperature adjusted according to maximum sensitivity for each individual compound (see Figure 6); discharge electrode 4000 V; grid electrode off.

repulsion of both positively and negatively charged species by the grid electrode reduces analyte signal intensity.

A deleterious effect on the response occurs when voltages (positive or negative) are applied to the grid electrode; the utility of the grid electrode in the operation of the DART source appears questionable.

Interestingly, Harris and Fernandez[14] have recently undertaken SIMEON calculations describing the sampling region of a DART source and concluded that the grid electrode potential should affect sensitivity because it determines ion mobility. However, our results (Figure 8) do not support such a model wherein ion sampling is influenced by ion mobility, as no trend in signal intensities with respect to the polarity or magnitude of the voltage applied to the grid electrode is evident.

CONCLUSIONS

DART has proven to be a versatile and robust technique, allowing fast and precise identification of a variety of organometallic compounds. The use of a N$_2$ discharge often favors

(14) Harris, G. A.; Fernández, F. M. *Anal. Chem.* **2009**, *81*, 322–329.
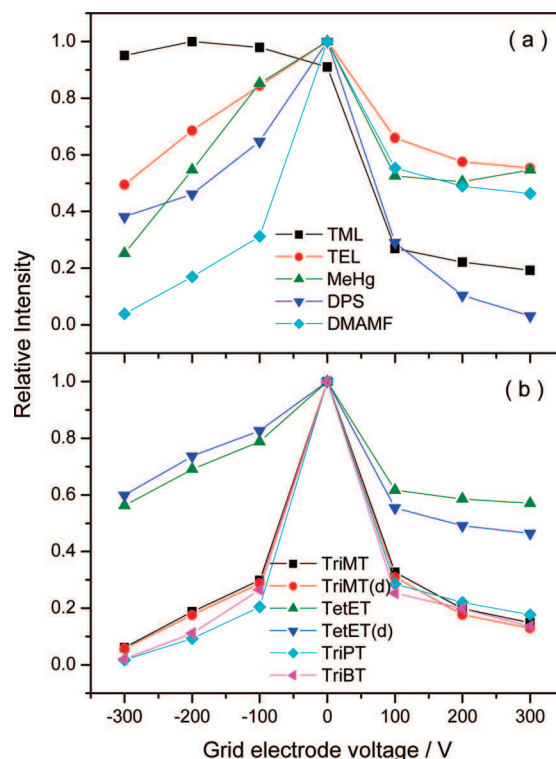
Figure 8. Effect of grid electrode voltage in the DART source on signal intensity for a series of organometallic compounds: (a) Fe, Hg, Pb, and Se compounds; (b) Sn compounds. "d" denotes a dimer species. Helium discharge used for TML, TEL, and MeHg (7.0 L min^{-1}); N$_2$ discharge (3.0 L min^{-1}) used for the remaining compounds. Conditions: gas temperature adjusted according to maximum sensitivity for each individual compound (see Figure 6); discharge electrode 4000 V; secondary electrode off.

detection of dimers, in contrast to results with the He plasma. A gas phase sampling approach, using the vapors swept from the head space above a pure compound, provides for a temporally stable signal which allows efficient evaluation of the influence of operating parameters of the DART source on response. The results obtained demonstrate the apparent participation of charged plasma species in the ionization process of all the species derived from the organometallic compounds investigated.