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**PHOTOCHEMICAL VAPOR GENERATION: A RADICAL APPROACH TO
ANALYTE INTRODUCTION FOR ATOMIC SPECTROMETRY**

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ABSTRACT

Photochemical vapor generation (PVG) is the newest subset of widely used vapor generation techniques to be coupled to atomic and mass spectrometries to provide enhanced analyte introduction efficiency. Improved detection power, minimization of potential spectral interferences and the promise of green chemistry serve as additional drivers. PVG has been successfully applied to the conventional suite of elements typically amenable to chemical vapor generation, such as As, Sb, Sn, Bi, Se, Te, Hg and Pb, as well as transition metals (Cd, Fe, Co, Ni and Os) and non-metals (I and Br). This article provides an overview of developments and applications since its inception in 2003, including consideration of needed hardware (UV photochemical reactor and phase separator designs), reaction mechanisms and products, interferences, as well as benefits and short-comings. While significant advances have been made over the past decade in expanding the scope of elements amenable to PVG, the way forward demands elucidation of reaction mechanisms to support optimization, enhance prediction power and provide comprehension and understanding of potential interferences. In this connection, speculations on ultimate limitations, needed developments and future outlook are also discussed. More applications to real-world samples are needed to sustain interest in the field and elicit further investment of research.

Keywords: Vapor generation; Photochemical vapor generation; Sample introduction, UV reduction; Analyte reduction, alkylation, hydridization and carbonylation.

INTRODUCTION

Trace element analysis invokes many definitions, from simplistic statements of determination of analytes in the range below 1 mg/kg to more broadly framed concerns encompassing consideration of analyte levels which are sufficiently low that the sample requires special handling, the matrix effects are substantial, the analyte signal-to-noise response (S/N) is small with the available measurement technique or the amount of sample available is very limited.¹ Increasing demands for higher throughput, improved data quality and enhanced detection power have resulted in laboratories embracing a preferential use of the inductively coupled plasma (ICP) as both an excitation (ICP-OES) and ionization (ICP-MS) source for quantitation of inorganic trace elemental and speciated mass fractions because of its wide (multi-)element capability, relative robustness, wide dynamic range, precision and generally simple, yet diverse, sample introduction systems. Nevertheless, with the exception of direct sample insertion techniques², the ICP requires sample introduction either *via* aerosolization, wherein test specimens must be converted to: (a) an aerosol of fine solid particles (achieved with arc/spark and laser ablation of materials in addition to electrothermal vaporization of solids/slurries and dried liquids); (b) an aerosol of fine liquid droplets (*via* thermospray, ultrasonic and pneumatic solution nebulization systems), or (c) a vapor (gas chromatographic effluents and volatile metal species synthesized using derivatization techniques).³⁻⁸ Despite solution nebulization being the most popular means of sample introduction, numerous studies have addressed its limitations; the resultant aerosol properties influence the thermal characteristics of the plasma, impacting sensitivity, precision, LOD and the extent of interference effects.³⁻⁸ Apart from post aerosolization processing, such as the use of heated spray chambers⁹, pre-evaporation tubes¹⁰, cryogenic and membrane desolvation systems¹¹, low-flow nebulizers to limit plasma loading (typically < 20-30 mg/min of water vapor)^{3, 4, 8, 12} or reliance on the torch integrated sample introduction system (TISIS)¹³, augmenting the performance of typical nebulizer/spray chamber systems is thwarted by the characteristically inverse relationship between the flux of analyte atoms delivered to the plasma and the efficiency of sample utilization as sample uptake rate increases.^{7, 8} Thus, attempts to augment S/N by increasing sample flux are met with diminishing returns due to enhanced aerosol density, increased droplet aggregation and loading effects in the spray chamber and plasma.^{7, 14} Keeping in mind that the goals of sample introduction are the

reproducible transfer of a representative portion of sample material to the atomizer cell with high efficiency and no adverse interference effects⁶, Bings *et al.*⁴ concluded that the ideal sample for the ICP would be in a gaseous form.

Expectedly, coupling analyte derivatization or vapor generation (VG) techniques to atomic spectroscopy sources provides a potential solution to this conundrum. Vapor generation may be defined as a process whereby volatile or semi-volatile analyte species are (physico-chemically) synthesized from non-volatile precursors (usually ionic or organometallic) to permit their subsequent transfer from a condensed phase to the gas phase. With high efficiency vapor generators, sample flow rates (i.e., analyte flux) can be substantially increased without perturbing generation efficiency. In principle, a VG manifold operating at 100 % derivatization efficiency with a sample flow of 5 mL/min could deliver a 125-250-fold greater flux of analyte to the plasma than a standard concentric nebulizer / cyclonic spray chamber system operating at 1 mL/min achieving 2 - 4 % efficiency, or a 166-fold enhanced flux compared to operating a TISIS coupled with a 30 μ L/min sample flow. As such, corresponding relative detection limits can be substantially improved over SN techniques.¹⁵

Apart from the obvious benefits that accrue from the above simple considerations, use of VG offers further advantages, as summarized in Table 1, foremost of which is that the target analyte is selectively separated from the matrix, which does not enter the source and hence does not contribute to potential physico-chemical matrix or spectral interferences. Admittedly, on balance, there are drawbacks to VG. Although the limited range of applicability, compatibility with specific matrices, species specific response and need for often potentially expensive and unstable reagents preclude widespread use, niche applications exist wherein its advantageous features have been exploited to optimal advantage.¹⁶

Over the course of some 50 years of development (following the classic application by Holak describing quantitation of As by generation of AsH_3 ¹⁷), the scope of analytical VG has continually advanced and now comprises chemical, electrochemical, sonochemical, thermochemical, photochemical and plasma mediated technologies. Many of these techniques have been relatively recently reviewed^{16, 18-26}, and almost all have been coupled to emission, absorption, fluorescence and mass spectrometry detection platforms. By far, approaches to chemical vapor generation (CVG) are the most diverse, viz. halide (As, Si), oxide (Os, Re, Ru),

carbonyl (Fe, Ni, Co), cold vapor generation (Hg, Cd), volatile chelate formation (Cr, Be, Co, Fe, Mn, Zn, Cu, Al, Ni, Mg, Yb, La, Eu and Y), oxidation (halogens) and alkylation reactions (with Grignard reagents, alkyl- and arylborates), as well as hydride generation (HG) for elements such as As, Sb, Bi, Se, Te, Ge, Sn and Pb. The latter technique remains the most popular and in recent years has expanded to encompass transition and noble metals (Ag, Au, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pd and Pt), although with relatively poor generation efficiencies and incomplete understanding of the nature of the resultant volatile species.^{27,28}

This review focusses on photochemical vapor generation (PVG). PVG has been successfully demonstrated with the conventional suite of elements typically amenable to chemical vapor generation, (such as As, Sb, Sn, Bi, Se, Te, Hg and Pb), as well as transition metals (Cd, Fe, Co, Ni and Os) and non-metals (I and Br). An overview of developments and applications of PVG since its inception in 2003^{29, 30}, including consideration of UV photochemical reactor design, reaction mechanisms and products, interferences, as well as benefits, short comings and possible future directions is presented. As PVG shares some common ground with plasma mediated vapor generation techniques, this area will also be briefly examined.³¹

Photochemical oxidation and reduction

Photochemistry encompasses chemical reactions that proceed under the influence of visible and/or ultraviolet light and the first law of photochemistry states that light must be absorbed by a compound in order for a photochemical reaction to occur. The rates of photochemical reactions are generally characterized by low apparent activation energies (a few kcal/mole, which often reflect the temperature dependence of secondary thermal reactions), but respond directly to the incident photon flux.

Photolytic and photocatalytic processes induced by UV irradiation have enjoyed a lengthy and widespread dichotomy of use in analytical chemistry.^{26, 32, 33} On the one hand, *photo-oxidation* of matrices for the destruction of organic matter by generated $\cdot\text{OH}$ radicals (typically), sometimes augmented by addition of $\text{S}_2\text{O}_8^{2-}$, H_2O_2 , Fenton reagent or O_3 , serve as the basis for many advanced oxidation processes in homogeneous systems while use of semiconductors (e.g., TiO_2 ,

ZnO, CdS) gives rise to heterogeneous photocatalytic oxidations; destruction of organometallic species prior to quantitation is also well-served by such green approaches to oxidation.

By contrast, *photoreduction* of toxic metals for water remediation and nanoparticle synthesis has been pursued for many years and touted for its industrial applications. In the natural environment, photo-mediated generation of volatile species from metal, metalloid and non-metallic elements occurs as solar radiation induces abiotic reduction and alkylation reactions in both the aquatic environment and troposphere, influencing the biogeochemical cycling of elements such as Hg, Br, I and S [e.g., ref.³⁴]

UV radiation comprises wavelengths between 100 and 400 nm, classified as UV-A (400 - 315 nm), UV-B (315 - 280 nm) and UV-C (280 - 100 nm). In the UV-C spectral region, sufficient photon energy is available for homolytic cleavage of C-C and many other bonds (e.g., 250 nm ~ 540 kJ mol⁻¹), as well as initiating mesolytic bond cleavage to yield radical-based reactions that lead to highly reducing environments in solutions containing low molecular weight carboxylic acids, alcohols and aldehydes.^{35, 36} Amongst reactive species are the highly reducing $\cdot\text{H}$, $\cdot\text{R}$, hydrated electron [$e^-_{(aq)}$], CO and carboxyl [$\cdot\text{CO}_2^-$] radicals.^{35, 37 - 40} Irradiation in the 200 - 100 nm range is typically undertaken under vacuum or purged conditions due to strong molecular absorption by atmospheric components and thus applications involving UV-C are fewer. However, proper design of the UV source itself has recently made the UV-C region a convenient and readily accessible laboratory tool with which to pursue PVG.^{41, 42}

The first demonstration of photo-reduction of an aquo-ion to a volatile hydride was published by Kikuchi and Sakamoto⁴³ in 2000, photocatalytic conversion of SeO_4^{2-} to SeH_2 occurred in the presence of TiO_2 in a dilute formic acid medium. The ramifications of this observation were soon realized by Guo *et al.*^{29, 30} and served to launch the field of PVG for trace element analysis in 2003. Utilizing chemistry based on homogeneous photo-reduction, SeCO , SeH_2 , $(\text{CH}_3)_2\text{Se}$ and $(\text{CH}_3\text{CH}_2)_2\text{Se}$ were generated in the presence of different low molecular weight organic acids. The reaction products, formed in high yield following exposure to a UV-C low pressure mercury discharge, were conveniently directed to atomic spectrometry sources for quantitation, enhancing sample introduction efficiency in a manner equivalent to classical CVG with

tetrahydroborate while suffering significantly fewer interferences from concomitant transition metals.

Over the past decade, a considerable number of PVG studies encompassing many additional elements (transition metals, halogens and semi-metals) have appeared but, despite substantial interest, the field of PVG remains in its infancy. As noted, photo-reduction processes can be implemented in a manner similar to CVG, not only for direct analysis, but with hyphenated techniques such as HPLC combined with post-column derivatization to provide speciation information as well. Uncharacteristically, reviews of this embryonic field began to appear only a short time after its inception,^{18, 20, 22, 23, 44} largely supported by inadequate information due to a limited applications base. More recently, and following publication of a considerably larger number of PVG studies, a more balanced outlook has surfaced⁴⁵, i.e., "...research in this area suggests that PVG is a highly efficient method of vapor generation for certain analytes, though matrix effects have yet to be fully evaluated to test the analytical utility of the technique for real samples".

Photochemical vapor generation

PVG confers a somewhat unique set of advantages in comparison to conventional CVG, as summarized in Table 2. Foremost amongst these are the elimination of the need for fresh and often expensive and unstable reductants, the ability to premix reagents with samples and simplify hardware requirements, as well as its broader range of application. On the other hand, because of its different mechanism of action, a new set of interferences arises from the presence of oxidants in the sample, as opposed to concomitant trace metals, which are deleterious to many CVG applications. These subjects will be discussed in more detail in subsequent sections.

Analytical applications of PVG require suitable laboratory hardware as well as a sample composition and reaction medium conducive to achieving efficient radical-driven reduction reactions which selectively target the analyte species.

PVG hardware. The simplest embodiment of a generic PVG laboratory system is presented in Figure 1. The basic principle of PVG for analytical application relies on generation of reducing

radicals from aqueous solutions of samples dosed with low molecular weight carboxylic acids (typically formic, acetic or propionic) by exposure to (primarily) UV-C sources. Although not widely used, alcohols and aldehydes have also exhibited some efficacy, at least for reduction of mercury.³⁶ An efficient phase separator serves to transfer the reaction products (volatile analyte species, CO, CO₂, H₂, CH₄)⁴⁶ from the sample solution to an appropriate source for detection using a flow of Ar or He.

The major hardware components of a PVG system comprise the UV-C source (photo-reactor) and the gas-liquid phase separator (GLS) which, in addition to the composition of the irradiated sample solution, account for all parameters impacting the efficiency of analyte derivatization. In general, design considerations and analysis of system performance should be based on the aspiration of providing the largest flux of analyte possible to the detector. Thus, when comparing sample introduction efficiency for PVG with that for solution nebulization, account must be taken of the impact of sample delivery rate on both the derivatization and phase separation efficiencies. High sample flow rates, providing delivery of the greatest flux of analyte, can be limited by the photo-kinetics of the reactions involved as well as the speed of phase separation of the products from the liquid phase. Since the photo-kinetics are dictated by the absorption coefficients of active components of the sample, the spectral quality of the source, relevant photon flux and irradiation time available with a given photo-reactor, whereas phase separation efficiency is governed by hydrophobicity of the analyte species, its diffusion length across the liquid phase (i.e., thin or thick film) and the concentration gradient across the gas-liquid boundary, it is evident that constraints arise as to how rapidly samples can be propelled through the PVG system. Several important design considerations thus need to be accounted for.

Continuous sample irradiation in flowing systems is by far the most efficient and frequently employed for PVG as heating of the sample is minimized during irradiation and thin-film conditions can be readily achieved.⁴⁷ As the absorption coefficient for liquid water lies in the range $10^3 - 10^5 \text{ cm}^{-1}$ at $< 170 \text{ nm}$, photon penetration depth is on the order of 1 mm at 185 nm ³¹, typically much shorter in aqueous solutions of carboxylic acids (cf. Figure 3). Moreover, flow injection processing of samples can be conveniently combined with stopped-flow conditions to increase the time available for exposure of the sample to the UV field.^{48, 49} Analyte reduction/derivatization is less efficient with batch reactors, despite being well-stirred, not only

due to the latter effect, but as well to the typically compromised ability to achieve rapid gas-liquid separation in such systems. Long exposure times needed to achieve good yields for some elements in batch systems give rise to increased probability of simultaneous photolytic *decomposition* of analyte species, in direct competition with photo-formation.^{41, 49-52} As a consequence, even in flow systems, an optimal UV irradiation time is generally encountered. Although thin-walled Teflon tubing is preferred for sample and gas transport lines due to its robustness, the sample suffers significantly diminished photon flux (intensity) as a result of the low UV-C transmission of this material compared to quartz (particularly synthetic quartz, needed to efficiently access the vacuum UV region, i.e., 184 nm).

Although high pressure mercury discharge lamps have been used to irradiate samples⁵³, these sources typically require forced air or water cooling and are inefficient in that they emit predominantly a continuous spectrum with superposed mercury emission lines, tending to heat the sample more efficiently than photolysing it, and are efficacious only as a consequence of their high power levels. The preferred design of photo-reactor comprises a low pressure discharge lamp dominated by the characteristic line spectrum of mercury. Typically, and for convenience of use, a quartz envelope shrouds the lamp, preventing ozone formation but limiting the output spectrum to the major emission lines at 253.7, 313.2, 365.0, 404.7, 435.8, 546.1, 577.0 and 579.1 nm while suppressing the intense 184.9 nm deep UV transition. Low power mercury discharge lamps are available from many suppliers with power ratings ranging from a few W (e.g., Analamp, available from BHK Inc.) to several 10's W (e.g., available from Cole Parmer) output, taking the form of pen lamps and inexpensive germicidal lamps, respectively. These sources are convenient in that the sample solution can be readily irradiated as it flows through quartz or Teflon tubing coiled around the exterior lamp envelope. Additional flexibility is available in that the length and inside diameter of this conduit can be user selected and, in concert with the flow rate of the sample, readily used to vary the irradiation or residence time of exposure of the sample to the UV source. Moreover, as noted above, the use of a thin film of sample exposed to the UV field serves to mitigate the effects of extraneous absorption of source intensity as it penetrates the liquid medium, thereby delivering the UV intensity with high efficiency and minimizing the need for enhanced irradiation time for the processing of colored (highly absorbing) samples.⁴⁷

Three further photo-reactor designs have found application for PVG, these being: a combined GLS and UV source comprising a pen lamp discharge mounted along the vertical axis of a cyclonic spray chamber to permit irradiation of the aerosol arising from a pneumatically nebulized sample⁵⁴; a commercial high-intensity, thin-film synthetic quartz flow-through photo-reactor that permits ready access to the 184.9 nm line without ozone generation⁴²; and deep UV (240-260 nm), low power (mW) LEDs.^{55, 56} Performance comparisons of different designs of photo-reactors and sources have been made.^{51, 54-58}

Rapid removal of the volatile analyte species from the irradiated solution constitutes an additional critical step since, as noted above, decomposition and resolubilization of the generated analyte species may occur. Clearly, the combination of UV source and spray chamber permitting irradiation of an aerosolized form of the sample⁵⁴ provides for both the thinnest film of liquid (i.e., μm -sized droplets) to be irradiated with highest efficiency, as well as the most effective means of phase separation since the vapor diffusion process rapidly occurs across a very thin liquid film and is further enhanced by the high phase concentration gradient arising from the flow of nebulizer gas (Henry's Law). The shortcoming of this design is the limiting and extremely short irradiation time (a few s for a 30-50 mL spray chamber supplied with a 1 L/min flow of Ar), necessitating fast photochemical kinetics, as well as a limitation on the supply flux of sample if aerosolization is to be supported. Some advantage can be taken of a nebulizer/spray chamber for fast phase separation by feeding the photolysed sample from a conventional reactor directly to a nebulizer.⁵⁹ This arrangement eliminates the aforementioned problem of short UV residence time, but does limit the of analyte flux to the detector due to the need to support aerosolization at relatively low flow rates. It is also noteworthy that use of nebulization systems and spray chambers negates one of the potentially major benefits of PVG/CVG, that the sample matrix is not introduced into the detection system. Apart from this unique system, both passive and active GLS designs have been employed.⁴⁹ Passive GLS relies on a flow of a thin-film of the irradiated liquid over a large inert surface in the presence of a counter-current of carrier gas. This approach works well for very hydrophobic analyte vapors but the flow rate of the sample is limited by the rate of phase separation (by diffusion), otherwise the sample solution is expelled to waste before separation can be efficiently completed. This problem is obviated with a GLS based on efficient mechanical sparging of the liquid by the transport gas before it is evacuated to waste and readily accomplished by directing the irradiated sample to/across a fritted disk through

which the gas is passed, efficiently stripping the analyte from solution. Examples of passive and active GLS units are described in ref⁴⁹.

Sample and generation media. In addition to the photo-reactor and GLS hardware, consideration of the chemical composition of the sample solution and added LMW carboxylic acids are significant variables impacting the PVG process. A rather brief review of these concepts is presented here as an in-depth examination is more appropriately reserved for subsequent sections relating to reaction mechanisms and interferences.

As noted earlier, not only has the presence of aldehydes and alcohols^{36, 60, 61} been shown capable of inducing PVG of mercury, but even diethyldithiocarbamate (DDTC)⁶² has served as an efficient reductant. Nevertheless, use of low molecular weight carboxylic acids, viz. formic, acetic and propionic, dominates due to their broad efficacy. Addition of these individual acids to the sample in concentrations ranging from 1- 50 % (v/v) is typical, and in some cases their mixture has proved beneficial^{63, 64}, as has been the addition of photosensitizers, including trace metals⁶³⁻⁶⁵ and other reagents.⁵⁸ Increasing the temperature of the reaction medium has, in some cases, been shown to enhance the yield of volatile analyte^{51, 56, 66}, but it is not clear whether this is due to enhanced derivatization efficiency or improved gas-liquid phase separation efficiency.^{67, 68}

Apart from the highly-reducing PVG media that accrues in the presence of carboxylic acids, advantage has been taken of simple photolysis of water to provide an *oxidizing* medium in which high generation efficiency of can be achieved⁶⁷, although OsO₄ has also been generated by PVG from a dilute solution of 5 % HNO₃.⁶⁹

The identification of PVG reaction products, including that of the volatile analytes as well as concomitant oxidation/reduction species, has generally been undertaken by direct GC-MS sampling of the effluent gasses from the photo-reactor or following cryotrapping.⁴⁶ Homolytic cleavage of the carboxylic acids used in reaction media yield hydrogen, carboxyl, methyl, ethyl, propyl and carbonyl radicals (ultimately forming H₂, CH₄, CO, CO₂, CH₃OH, C₂H₆) which reduce, hydrogenate, alkylate and carbonylate metal ions to produce reduced, hydrided, alkylated or carbonylated products. Table 3 identifies the principal analyte species generated. It is clear that irradiation of a formic acid medium is capable of giving rise to reduced (Hg⁰), hydrided and

carbonylated species, as commonly found in nature, whereas acetic acid further permits methylation to occur and propionic acid can give rise to ethylated products. It should be noted that when using propionic acid it is possible to generate a significant mixed population of ethyl, methyl and hydrogen radicals such that all alkylated forms of a given element may be present in the PVG products. A similar pattern holds when acetic acid is used. To date, no specific identification of Sn, Sb, Pb, Cu or Os species arising from PVG has been reported; one may speculate that these species may be: SnH_2 , $\text{Sn}(\text{CH}_3)_2$ and $\text{Sn}(\text{C}_2\text{H}_5)_2$; SbH_3 and $\text{Sb}(\text{CH}_3)_3$ and $\text{Sb}(\text{C}_2\text{H}_5)_3$, PbH_4 or $\text{Pb}(\text{CH}_3)_4$ and $\text{Pb}(\text{C}_2\text{H}_5)_4$, and OsO_4 . Identification of the unstable species of Cu⁷⁹ remains beyond the realm of speculation at this time.

A broader suite of elements is amenable to PVG that can be accomplished with hydride generation, as the former also includes those from the latter category.⁸⁰ Moreover, the high generation efficiencies, summarized in Table 4, lead to significantly enhanced sample introduction efficiencies and corresponding limits of detection in comparison to solution nebulization, more so because the flow rates of sample delivered to the source can readily exceed those amenable to efficient aerosolization with a conventional nebulizer/spray chamber, thereby further enhancing the flux of analyte delivered.

PROPOSED MECHANISMS OF PVG

A comprehensive approach to a mechanistic interpretation of chemical hydride generation was conceived some 40 years after its first application^{21, 25}; it is possible that this will ultimately be achieved with PVG, if interest in the technique can be sustained. Apart from a single computational model based on photochemical generation of a reactive ketene (CH_2CO) intermediate generated in acetic acid⁸⁵, there is a general consensus in the literature that PVG is the result of radical reactions initiated by the photolysis of carboxylic acids and ligand-to-metal charge transfer reductions and oxidations, as these are consistent with the majority of experimental data, including the identity of the resultant species and the impact of experimental parameters.⁴⁶ As noted earlier, the generation of powerful carboxyl radicals [$\text{CO}_2^\cdot$] enables a system containing oxidizing and reducing radicals ($\text{OH}^\cdot$, $\text{H}^\cdot$ and $e^-_{(aq)}$) to be converted into one

that is dominated by reduction processes.^{38, 39, 86-89} A brief review of the proposed mechanisms of PVG is presented in the following, the reader is referred to original publications for a more in-depth treatment of individual analytes.⁴⁶

Photolysis of a solution of formic acid yields a complex mixture of reductants:

This series of reactions accounts for the various gas phase end products of photolysis, viz. a mixture of H₂, CO and CO₂. When higher order carboxylic acids such as acetic (R = CH₃) and propionic (R' = C₂H₅) are used, these give rise to $\cdot\text{R}$ and $\cdot\text{R}'$ radicals yielding the experimentally observed CH₄ and readily accounting for the various volatile analyte species summarized in Table 3. Interestingly, Adams and Hart⁸⁶ discussed photolysis and radiolysis of aqueous

solutions of formic acid over 50 years ago, showing that the yield of CO increased with increasing concentration of HCOOH, elevated temperature, decreased pH and decreasing wavelength, all experimental parameters that have found impact with PVG studies and certainly playing a role in the generation of Ni(CO)₄ and Fe(CO)₅.^{66, 76, 81}

Despite many years chronicling studies of transition metal assisted oxidation, decarboxylation and alkyl transfer reactions which occur in solutions of carboxylic acids, the photochemical literature is, unfortunately, essentially devoid of observation / discussion of metal PVG phenomena, as evident in a recent review of the field,³⁵ which is frequently characterized by the overall ligand-to-metal charge transfer (LMCT) reactions:

Few instances of metal-carbon bond formation have ever been reported, as in the case of a conjectured intermediate of Ni⁺ (NiCO₂) in a solution of irradiated formic acid.⁹⁰

Sturgeon and Grinberg⁴⁶ attempted to formulate a comprehensive model for PVG based on reactions 1-11, the pH dependent formation of metal carboxylates, LMCT reductions and charge transfer to solvent (CTTS) oxidations (for the halogens).⁹¹ As noted earlier, the first law of photochemistry dictates that photons must be absorbed by a compound in order for a photochemical reaction to arise; reactions are similar whether they occur in the liquid or vapor phase. The rates of photochemical reactions are generally characterized by low apparent activation energies (a few kcal/mole, which often reflect the temperature dependence of secondary thermal reactions). Figure 3 displays UV absorption spectra of dilute solutions of formic and acetic acids, showing significant absorption of radiation corresponding to $\pi \rightarrow \pi^*$ transitions below 250 nm. It may be relevant that absorption by formic acid occurs to a greater degree at 254 nm than does acetic acid, as this may account for the favorable increase in PVG yields of several analytes when a mixture of these acids is used as the generation medium as opposed to only acetic acid.^{63, 64} In this regard, formic acid may serve as a sensitizer for the reaction. Figure 4 shows the UV-Vis absorption spectra of solutions of 200 mg/L Fe(III) in either 30 % formic or acetic acids adjusted to pH 2 (air reference cell), illustrating the differing LMCT bands of the different carboxylate complexes and their clear overlap with emission lines from low pressure Hg photo-reactor sources.

As an example, Baxendale and Bridge⁹² investigated the photoreduction of ferric compounds in 3 % formic acid and reported optimal quantum yield in the narrow pH range 2-3.5. Interestingly, this also exactly corresponds with optimal pH for PVG yield of Fe(CO)₅.⁸¹ A proposed LMCT reduction:

may constitute the beginning of a cascade of subsequent reductions:

ultimately leading to the formation of Fe⁰ and successive attack by CO in the reaction medium to generate volatile Fe(CO)₅. Similar sequences may be envisioned for Ni(II) and Co(II). It is noteworthy to comment on the observation that optimal PVG conditions also include sample pH.^{76, 81} Generally, most researchers have assumed that as the pH is lowered, decreased response occurs because of competitive re-oxidation or solubilization/destruction of the derivatized analyte species before it has an opportunity to escape to the gas phase. In light of the above, it is clear that LMCT reactions may be key to several processes and thus require an optimal pH for ligand complexation to occur. Alternatively, it should also be recognized that proton donors in solution (such as phosphate and ammonium species) may react by converting needed solvated electrons into hydrogen atoms⁹³, thereby shutting down important electron reduction mechanisms as the acidity increases.

Mercury was one of the first elements to be subjected to PVG using formic acid as a reductant⁷⁰ and remains, along with several organometallic Hg species, the most frequently studied, as it is relatively easily photo-reduced in the presence of alcohols and aldehydes³⁶ as well as undergoes sonolytic⁹⁴ and thermochemical⁵⁶ reduction in carboxylate media. Zhang⁹⁵ has reviewed the literature devoted to photochemical redox reactions of mercury in the environment. In the simple case of Hg(II), typically present as the chlorocomplex, several possible reactions can be envisioned, including a primary photochemical process involving a LMCT reduction:

It is noteworthy that the UV-Vis spectrum of an aqueous solution of mercuric chloride shows significant broad attenuation of UV starting at ~ 260 nm, peaking at 205 nm and continuing down to near 180 nm. In the presence of 5% (v/v) acetic or formic acids, which also yield intense absorption peaks in the UV at ~ 230 and 238 nm, respectively, the ligated complexes could also give rise to LMCT reductions such as:

A similar set of reactions can occur for species such as methylmercury chloride, which also undergoes PVG in the presence of formic and acetic acids:

Compelling evidence for such radical-based reactions was provided by Yin *et al.*⁶¹ who demonstrated that oxidation of mercaptoethanol in the reaction medium resulted in production of a cyclic disulfide ester with corresponding reduction of both inorganic and methylmercury species.

Selenium was the first element to be investigated for analytical purposes using PVG.^{29, 30} As noted earlier, the study was inspired by a report from Kikuchi and Sakamoto⁴³ who discussed the photochemical reduction of selenite in the presence of TiO_2 catalyst to generate H_2Se from solutions of formic acid. The catalyst was subsequently found to be unnecessary for PVG of Se(IV) and, in the presence of formic acid, both SeCO and SeH_2 were detected^{29, 30}, whereas with acetic and propionic acids, dimethyl- and diethyl-selenides, respectively, were synthesized. Formation of these compounds is in accord with expectations for radical-based reactions arising from the systems discussed above. Sturgeon and Grinberg⁴⁶ proposed two possible scenarios to account for the PVG of Se(IV) ; a redox sequence involving release of a hydrated electron by

photolysis of HCO_2^- (eqn 2) and a cascade sequence of nucleophilic attacks by $\cdot\text{R}$ and rearrangements, as depicted in Figure 5:

or:

Other elements, such as As, Sn, Sb and Pb, may also undergo similar $e^-_{(aq)}$ reduction sequences (as outlined for Pb(II) by Pospisil *et al.*⁹⁶), or nucleophilic attack.

Se(VI) is not amenable to PVG, possibly because it possesses no free lone pair of electrons to permit initiation of nucleophilic attack by $\cdot\text{R}$ radicals (cf. Figure 5). Nevertheless, PVG of selenate has been successful, but only through the intervention of titania as a photocatalyst.⁴³ Following UV photon absorption by TiO_2 , an electron is promoted to the higher energy conduction band, leaving a positively charged hole in the valence band, as schematically illustrated in Figure 6. Amal and colleagues^{97, 98} have investigated this phenomenon in detail; using Raman and other techniques they concluded that formic acid as well as Se(IV) and Se(VI) adsorb onto TiO_2 . Formate is an efficient hole scavenger which gives rise to reducing radicals by scavenging $\cdot\text{OH}$. A series of reactions was proposed:

In a similar vein, photocatalytic reduction of mercury has been undertaken in the presence of TiO_2 with speculation that direct reduction by e_{cb}^- occurs to liberate Hg^0 .³⁶

Implementation of photocatalysts has been achieved using both heterogeneous and homogeneous systems. In the former, the added TiO_2 (typically nano-anatase) is suspended in the sample solution while exposed to the UV field. Typically, no more than a 1 g/L slurry of TiO_2 is employed, sufficient to confer photocatalytic activity while not impairing transmission of the UV flux through the sample.⁹⁹ Use of semiconductor $\text{TiO}_2/\text{ZrO}_2$ and ZrO_2 photocatalysts has been successfully developed for generation of H_2Se from both Se(VI) ¹⁰⁰ and mercury species.¹⁰¹ These photocatalysts possess greater band gaps than TiO_2 (5.0 eV) and thus should prove more efficient for reduction. Jia *et al.* have demonstrated the efficacy of photocatalysts based on metal organic frameworks (MOFs), crystalline hybrid inorganic/organic solids comprising metal (oxide) clusters interconnected by polydentate organic linkers.^{102, 103} Their ease of synthesis, porosity, high surface area and efficiency for reduction of Se(VI) point to an attractive alternative for TiO_2 . Most recently, metal-free g-3N4/CQDs (carbon nitride/carbon quantum dots) composites have been synthesized and applied to visible light source PVG of Hg .¹⁰⁴ The quest for ever more efficient photocatalysts continues.¹⁰⁵ Homogeneous application of TiO_2 photocatalyst can be conveniently accomplished by its physico-chemical immobilization on the interior wall of quartz tubing used to expose the sample to the UV field^{68, 106}, eliminating the problems encountered with its sedimentation when slurry preparations are used.

Apart from use of physical photocatalysts to enhance the efficiency of PVG, several recent reports of homogeneous “sensitizers”, concomitant metal ions endogenous to, or spiked into, the sample solution⁶³⁻⁶⁵ as well as other reagents⁵⁸, have appeared that bestow enhanced PVG efficiency for some analytes. In the case of the metal ions, it may be speculated that addition of Fe, Cu, or Ni or their mixtures may alter the photo-absorption spectrum of the sample and/or change the kinetics of decarboxylation reactions as well as even alter the products of the

reaction.³⁷ The presence of Fe(III), for example, may promote production of $\cdot\text{OH}$ radicals through simple LMCT processes¹⁰⁷ which subsequently alter the cascade of reactions leading to $\cdot\text{CO}_2^-$ as expressed by equation 5, thereby altering the reduction capacity of the sample. Unfortunately, the field is not sufficiently developed to be able to offer more concrete reasons for such observations and significantly more data are required in order to interpret such results.

Iodine was the first non-metal successfully subjected to PVG^{74, 108} for analytical purposes. In this respect, it is significantly different from the numerous metals that have been examined in that photolysis of iodide and iodate solutions containing low molecular weight organic acids leads to an *oxidation* reaction. Studies undertaken by Kloepper *et al.*⁹¹ have pointed to an initially excited state (*) populated by charge transfer to solvent (CTTS), evident in Figure 7. Rapid destruction of the CTTS state as the solvent rearranges the charge density leads to ejection of the electron into the solvent:

The concept of “cage” reactions arises¹⁰⁹ wherein the iodine atom-electron pair constitutes a loosely bound moiety which can either recombine or, through diffusion, interact with different partners to form the final product:

where $\cdot\text{R} = \cdot\text{H}$, $\cdot\text{CH}_3$ or $\cdot\text{C}_2\text{H}_5$ as derived from photo-decarboxylation reactions of the added carboxylate ligands. Clearly, if $\cdot\text{H}$ combines with $\cdot\text{I}$ to form HI, the product remains dissociated in solution and thus no PVG volatile product is detected using HCOOH media whereas volatile compounds are readily released from CH_3COOH . Similar reaction mechanisms can be invoked for bromine.⁷⁵

This mechanistic model for PVG has been offered in an attempt to provide a framework to entice interested researchers to more closely evaluate these mechanisms, use them as a guide to further

this field and to possibly minimize or control interferences by application of some of the basic principles. Significantly more information is needed before an understanding of equally complex issues relating to the temperature dependence of PVG yields and the role that catalysts and “sensitizers” play in promoting the photochemistry as these may influence the means by which insightful advantage can be used for the design of photo-reactors and manipulation of sample composition to guide method development.

INTERFERENCES WITH PVG

One of the more attractive features frequently ascribed to PVG (Table 2) is a reduction in interferences from concomitant elements when compared to that suffered by classical CVG techniques. Comparable vapor generation efficiency was reported for Se(IV) at up to 10^2 -fold greater concentrations of Cu(II), Co(II) and Ni(II) than typically tolerated with HG.²⁹ Nevertheless, following a further decade of study, it is now recognized that a new suite of relatively severe interferences occurs with PVG that is typically foreign to HG.

Consistent with a radical mechanism of PVG attained under reducing conditions by the generation of $\cdot\text{CO}_2^-$, $\cdot\text{H}$ and $\cdot\text{R}$ radicals along with $e^-_{(\text{aq})}$ during photolysis of solutions of LMW carboxylic acids, a number of interferences arise from transition metal ions, notably copper, iron, nickel and cobalt, as well as common oxidants, including dissolved oxygen, nitrate and nitrite ions. Whereas the former group of interferences give rise to both suppressed as well as enhanced yields of photochemically generated analytes when present at low mg/L concentrations^{45, 49, 64, 66, 110}, that for the common anionic oxidants, including chloride, can manifest themselves typically in the low mM concentration range and are always suppressive.^{29, 84}

Although their specific mechanism of action remains elusive at this time, the positive impact of transition metals may derive from their possible concurrent role as sensitizers for accelerated photo-oxidation of carboxylic acids, as noted earlier, sometimes with specificity, e.g., Fe(III) enhances the rate of oxidation of HCOOH 100-fold more than it does that of CH₃COOH.³⁷ Suppressive interferences, on the other hand, may arise because such metal ions serve as simple oxidants, potentially inhibiting analyte reduction reactions by consuming needed species of reducing radicals^{89, 96}.

It is noteworthy that contradictory observations can be found in the literature concerning the severity of interference imparted by the presence of endogenous or added trace elements. As an example, Campanella *et al.*⁵¹ reported significantly greater interferences from Cu(II), Ni(II) and Fe(III) than noted by Guo *et al.*²⁹ during PVG of Se(IV), possibly due to their use of much lower concentrations of formic acid in the reaction medium as well as potentially different photo-reactors which influence the available photon flux and reaction temperature. In the case of Cu(II), interference was ascribed to the impact of reduced Cu metal being formed, consistent with equations 36 and 37.

Dissolved oxygen, along with NO₃⁻, NO₂⁻ and Cl⁻, are recognized quenchers of radical-based reactions due to their affinity for e⁻_(aq) and [•]H and [•]R.^{46, 109, 111, 112} Nitrate is a concomitant anion in many sample solutions prepared for instrumental analysis as it is frequently derived from nitric acid used to solubilize test samples or serves as a preservative for trace element content in solutions. Natural “contamination” of environmental aqueous samples by NO₃⁻ is unlikely to present a major problem in this regard because concentrations are typically in the uM range, some 2 orders of magnitude below which it constitutes a concern for PVG. Figure 8 illustrates the relative suppression of PVG response from a 10 ng/mL solution of Se(IV) in 4 % acetic acid in the presence of these anions.¹¹³ Although never deliberately added to samples, nitrite is a product of the photoreduction of NO₃⁻.¹¹⁴ It is evident that PVG efficiency is much more sensitive to the presence of NO₂⁻ as it exhibits similar suppressive effects at 10 - 20-fold lower concentrations than does NO₃⁻. This may suggest that it is nitrite, rather than nitrate, that is directly responsible for the interference effects noted in PVG systems. Both anions participate in

the complex redox equilibria operative in a PVG system, consuming photogenerated electrons ($e^-_{(aq)}$) and $\cdot\text{H}$ radicals^{112, 114}, thereby making them less available for reduction of analyte species:

Additionally, nitrite may cyclically photoregenerate nitrate (Eqn 46) by reaction with generated peroxide (arising from $\cdot\text{OH}$). Note that reactions 42 and 43 create oxidizing $\cdot\text{OH}$ radicals³³ which can rapidly react with $\cdot\text{H}$ species to effectively serve as a source of interference for PVG of hydrogenated analyte, such as SeH_2 . This may explain the impact of added NO_3^- on enhancing the amount of SeCO relative to SeH_2 produced when PVG of Se(IV) is undertaken in formic acid media.²⁹ Additionally, NO_3^- can react with the generated hydroxyl radical to produce a nitrate radical which will result in oxidizing peroxide species.¹¹⁵ Reactions 33 - 37, which may also be involved in the sequential reduction of *analyte* species leading to their PVG, may be suppressed in the presence of much higher (mM) concentrations of NO_3^- and NO_2^- as a consequence of their direct oxidation of the analyte.⁸⁹

While it is relatively easy to remove dissolved gases from sample solutions, it is a difficult matter to eliminate or mask oxidizing anions and trace metals.¹¹³ As a general principle, nitric acid should be avoided or minimized when PVG is contemplated for quantitation. Strategies such as direct use of formic acid¹¹⁶ or tetramethyammonium hydroxide (TMAH)⁸⁴ should be considered for the solubilization of tissue samples. Microwave assisted dissolution of many matrices can be efficiently accomplished using minimal volumes of concentrated acids. Further minimization of the amount of oxidizing acids required can be achieved by using microwave assisted digestion and resorting to use of hydrogen peroxide in the reaction medium¹¹⁷, reliance on use of more dilute acids¹¹⁸, microwave induced combustion techniques¹¹⁹ and extreme temperatures and pressures available with the Single Reaction Chamber.¹²⁰ Alternatively, evaporation of concentrated residual acids present in digested samples and resolubilization of the residue in an (alternative) dilute acid, although time consuming, also provides an effective approach to sample preparation which minimizes interference from nitrate media.^{15, 51, 66, 121} Under favorable circumstances, amelioration of suppression of response from endogenous trace elements may be accomplished by addition of chelating agents¹¹³, but if significant molecular absorption from metal aquo- and carboxylate-complexes arises (cf. Figure 4), the physical attenuation of available photon flux may seriously degrade the kinetics of PVG of the analyte.

Provided the PVG yield remains advantageous, use of isotope dilution techniques for quantitation when MS detection is available serve to circumvent interference effects when multi-isotopic analytes are being considered^{15, 23, 63}, otherwise matrix matched standards, best implemented *via* use of the method of additions, must be considered.

ANALYTICAL APPLICATIONS OF PVG

Earlier reviews^{18, 20, 22, 23} have summarized applications of PVG, at least up until 2011. By far, the most frequent targets have been mercury and selenium, focusing on determinations of both their total and speciated forms.¹²² Although applications of PVG remain relatively sparse, they have increased considerably in the past 6 years to include: osmium in tap and natural waters^{67, 69}; iodine and bromine in mineral water, simulated seawater as well as sediments and biological tissues^{75, 108} and coal⁷⁵; tin in lake water¹²³; copper in biological tissues⁷⁹; cobalt in biological

tissues⁴⁹, natural waters⁸², Chinese medicinal products¹²¹ and alcoholic beverages¹²⁴; tellurium in alcoholic beverages¹²⁴; lead in natural waters¹¹⁰, seawater¹²⁵ as well as sediments and river water⁶⁵; antimony in natural waters⁶³; arsenic in surface waters⁶⁴ and seawater¹²⁶; iron in biotissues and river water^{15, 81, 127}; nickel in sediment⁶⁶, biotissues¹²⁷, nanotubes¹²⁸, Chinese medicinal products¹²¹, alcoholic beverages¹²⁴, urine¹²⁹, river water^{15, 66}, tap water and soils¹³⁰; mercury in gasoline⁶⁰, ethanol¹³¹, glycerin¹³² and naphtha¹³³, alcoholic beverages^{53, 134}, biological tissues and hair^{61, 62, 84, 94, 127, 135 - 138} cosmetics¹³⁹, vaccines^{140, 141}, vinegar¹⁴², waters^{42, 50, 70, 71, 94, 143, 144}, petroleum production water¹⁴⁵, sediments¹⁴⁶ and seafoods¹⁴⁷; as well as selenium in table salt⁶⁸, drinking water and wastewater^{68, 148}, biological tissues^{15, 148}, dietary supplements^{149, 150}, natural waters⁹⁹, river water¹⁵¹ enriched yeast¹⁰⁰ and freeze-dried urine.⁵¹

As with other vapor generation techniques, PVG has been utilized for both analyte preconcentration^{42, 50, 60, 62, 66, 122, 137, 143, 148, 151, 152} as well as species-specific quantitation for mercury and selenium.¹²² Speciation information has been achieved by making use of photo-reactor source characteristics^{45, 55, 56, 70}, solution chemistry^{62, 84}, photocatalysts^{97, 99-102}, as well as conventional HPLC separations^{70, 71, 99, 101, 153, 154}. Quantitation strategies have been based on external calibration standards, matrix matched and standard additions approaches, as well as isotope dilution.^{15, 23, 63, 135, 139} The advantages of the latter are clear when PVG yields are affected by endogenous matrix species in the sample solutions that contribute to radical quenching, sensitizing and simple source attenuation due to colored absorbers.

PLASMA MEDIATED VAPOR GENERATION

Perhaps closely allied with PVG approaches, due to a potential common mechanism of action, are techniques that may be described as plasma mediated vapor generation. DC and high frequency non-thermal plasmas in He and Ar discharges are rich sources of UV radiation which can serve the same role as conventional photochemical reactors in that numerous free radicals can be generated in sample solutions exposed to such plasmas.¹⁵⁵ The most useful variants are atmospheric pressure glow discharges, such as the solution cathode^{155, 156}, and dielectric barrier discharges.^{157, 158} With the former discharge, the plasma is in direct (electrodeless) contact with the liquid sample, thereby also permitting potential electrochemical reactions to occur (as with electrochemical hydride generation¹⁹). Electron transfer reactions at the interface have been

increasingly studied¹⁵⁹⁻¹⁶² in relation to the generation of volatile species and Bruggeman *et al.*³¹ have recently reviewed such discharges and presented a roadmap for their future implementation. Both sources are compact, operate at high efficiency and have been used to advantage for metal vapor generation, offering the same green chemistry as PVG, thereby complementing standard PVG approaches.

It appears that Zhu *et al.*¹⁶³ were the first to report on the phenomenon of cold vapor generation of mercury from both inorganic and organo-mercury compounds from a *solution cathode* glow discharge (SCGD). The background electrolyte was 0.1 M HNO₃ although the presence of low molecular weight organic acids, such as 1 % formic, enhanced the generation efficiency such that it was superior to a conventional CVG approach employing reduction by SnCl₂. Several mechanisms were proposed, including simple solution sputtering (unlikely to selectively enhance vapor yields) and a thermal mechanism (similar to thermolysis action reported for mercury reduction⁵⁶) as well as the intervention of radicals and free electrons. Significant interference was evident from the presence of chloride, which in hindsight, is to be expected from the viewpoint of radical quenching as well as Hg-complex formation. Decker and Webb¹⁵⁶ have speculated on the mechanisms operative in SCGD but were unable to unequivocally identify specific modes of action, one of which was suggested to be PVG. Subsequent further work from Zhu's laboratory further coupled the SCGD source to demonstrate vapor generation of iodine¹⁶⁴ from pH 2 HNO₃ with an estimated efficiency of 60 %; for the speciation of mercury when combined with HPLC using a mercaptoethanol mobile phase¹⁶⁵, and the vapor generation of Os¹⁶⁶ from pH 1 HNO₃ with an estimated 51 % efficiency. Note that for iodine and osmium generation, oxidation is required, consistent with PVG mechanisms, as evidenced by equation 31).

The application of flow injection sample processing coupled with single drop SCGD vapor generation was demonstrated by Zheng *et al.* for detection of total mercury in fish tissues¹⁶⁷ as well as Cd and Zn in samples of hair and paramecium cells¹⁶⁸ by establishing a glow discharge in an Ar/H₂ mixture supporting a plasma established between the tip of a tungsten electrode and a 5-20 μ L liquid droplet. The low power (12 W) plasma was sustained using a compact ozone generator operating at 4 kV and 20 kHz. The typical experimental arrangement is depicted in Figure 9. Mercury species were extracted from mg-sized tissue subsamples supported on multi-

walled carbon nanotubes using an L-cysteine/HCOOH mixture, which dramatically enhanced response. This was attributed to the increased reduction capacity of radicals generated from the formic acid by the glow discharge. Atomic fluorescence provided an absolute limit of detection of 0.2 pg. High generation efficiencies reported for Cd and Zn (90 and 80 %, respectively) were achieved during the 10 s that the plasma discharge was used to process the liquid droplet and yielded absolute detection limits of 0.2 and 2 pg for Cd and Zn, respectively. Although high “sample introduction” efficiency is claimed, it is in reality high vapor generation efficiencies that were realized.

Most recently, Liu *et al.*¹⁶⁹ demonstrated the advantage of a *solution anode* glow discharge arrangement for the plasma mediated vapor generation of volatile molecular species of both Zn and Cd from a pH 2 medium of HCl. Sensitivity was enhanced 10-fold over the conventional SCGD arrangement. It was postulated that electron transfer reactions occurred at the interface of the (550 V, 10 mA) 7 W DC microplasma and the liquid surface. A subsequent study using the same type of apparatus¹⁷⁰ reported on the generation of volatile molecular (as well as atomic for Cd) species of Cd and Zn when the sample solution was introduced into the cathode compartment which housed a stainless steel capillary through which an Ar/H₂ mixture was passed to sustain a plasma between the tip of the capillary and the sample solution surface. A pH 3.2 HCl medium was used for samples and analyses of stream sediment and rice reference materials was undertaken for Cd along with a simulated water sample for Zn. Interferences from concomitant species necessitated the use of the method of additions for quantitation of Cd in the stream sediment.

Dielectric barrier discharges (DBD) are finding increased use as low power, inexpensive and simple sources for optical spectrometry.^{141, 158} Attention has recently turned to their potential use as sources for vapor generation. The first such applications of a DBD to replace a discrete photo-reactor appeared in 2011.^{171, 172} Hou's group¹⁷¹ employed the DBD source to reduce Hg(II) in dilute solutions of formic, acetic or propionic acids by simply pumping the sample solution (at 2 ml/min) through the concentric volume defined by a powered copper electrode encased in a dielectric quartz tube and that of an outer quartz tube wrapped in a counter electrode of copper foil. An Ar plasma formed in the kHz high-voltage 20 W discharge provided an intense UV spectrum with which to irradiate the passing sample. The Hg⁰ vapor so formed in

this PVG system was phase separated in a GLS and directed to an ICP for detection in emission mode. The research group of Zhu *et al.* has also actively pursued the use of the DBD for vapor generation over the past few years. They utilized an approach similar to that of Zheng *et al.*¹⁷¹ Inorganic-, methyl- and ethylmercury were successfully reduced to Hg^0 by subjecting a thin-film of the sample prepared in 1 % formic acid to the DBD plasma.¹⁷² This was accomplished by manually dipping the quartz encased copper powered electrode into the sample solution and withdrawing an $\sim 6 \mu\text{L}$ volume of liquid which would form a uniform thin-film on its surface. The sample bearing electrode was then inserted into the DBD assembly and power applied to establish a 5 W discharge. Total mercury was determined in freeze dried urine and tuna fish reference materials. In a companion paper published the following year¹⁷³, reduction of mercury as thiomersal in samples that were again manually administered ($\sim 8 \mu\text{L}$) onto the glass sheath surrounding the powered electrode by physically dipping it into the sample solution and inserting it into a 7 W Ar DBD plasma was reported. The same group generated volatile Cd species (presumed to be CdH_2)¹⁷⁴ based on a flow-injected volume ($300 \mu\text{l}$) of a pH 7 aqueous sample to create a flowing thin-film of liquid over the powered electrode of a DBD supporting an 18 W Ar/ H_2 plasma for quantitation of Cd in natural water and a rice reference material. This was shortly followed up by a second such study which detailed the production of a volatile Zn species¹⁷⁵ based on a similarly constructed 25 W He/ H_2 DBD plasma. More recently, Zhu's group has improved the performance of their earlier approach to Cd vapor generation¹⁷⁴ by the addition of non-ionic surfactants to increase the reaction kinetics and improve product transport efficiency for the determination of both Cd and Hg in natural water reference materials.¹⁷⁶ Subsequently, they incorporated an HPLC into the system to permit speciation of Hg for its determination as inorganic-, ethyl-, and methyl-mercury in a tuna fish certified reference material.¹⁷⁷ Figure 10 illustrates the set-up for a thin-film dielectric barrier discharge plasma-VG system.

A somewhat more elegant design of such a source was described by Yang *et al.*¹⁷⁸ wherein a sample was nebulized into a spray chamber from which the aerosol was directed through an Ar/ H_2 DBD and transported to an atomic fluorescence detection system. Hydrogen was required to yield signals from As, Te, Sb and Se with the suggestion that hydride generation had occurred within the plasma discharge. The potential shortcoming of nebulized solutions is, as mentioned

earlier, the entry of all sample components into the source and not simply the selective gating of the analyte, which perpetuates potential matrix and spectral interferences.

These approaches to PVG remain to be further explored and applied to more elements but are limited by the apparent low flow rates of sample solution that can be accommodated by the DBD reactors. Nevertheless, they provide an attractive venue for field deployment as advantage can be taken of their small size, high sensitivity, minimal power requirements and ease of integration into miniaturized spectrometer detection platforms. The same arguments obviously hold for use of atmospheric pressure glow discharges as PVG reactors as well as conventional PVG systems.¹²⁷

CONCLUSIONS AND OUTLOOK

Much of the “low hanging fruit” in this area has now been harvested, although an empirical push to broaden the list of elements amenable to PVG remains a relevant task. Suitable targets include Mo and W (volatile carbonyls of W and Mo have been identified in landfill gasses¹⁷⁹), Cr and Cl. The latter analyte provides an example where research conducted in ancillary fields¹⁸⁰ may provide insight on development of successful PVG approaches that circumvent the limited direct rationale now in use.

Reaction products of PVG appear to be accounted for based on reductions and radical based reactions which are fundamental to photochemical processes. These also appear to account for the effects of known interferences and help explain the impact of photo-reactor parameters on generation efficiency. Nevertheless, an in-depth understanding of the mechanisms of PVG should render predictive power to this endeavor and potentially result in control over known interferences. Such achievements will impact not only the ultimate possibilities of how the future of this field may unfold, but also lead to the attainment of robust conditions for sustainable high-yield generation of analytes from a plethora of matrices. It is evident that the traditional tools of photochemistry need to be applied to this new area of study¹⁸¹, including ESR for detection of radicals in solution, actinometry to assess photochemical efficiencies and stop-flow transient UV-Vis absorption spectra to provide the evidence needed to support the existence of intermediates such as free electrons and other species proposed herein. Additionally, more widespread use of electrospray-MS may prove useful for the detection of quasi-transient

intermediates in solution produced during photolysis.⁷³ Clearly, contributions from photochemists and inorganic chemists are needed in a multidisciplinary approach to support the analytical chemistry community in this endeavor.

Despite the need for additional mechanistic information, systematic investigation into the control/suppression/compensation of interferences, an expanded applications database and enhanced elemental coverage, the complementary nature of PVG positions it for a continuing role in ultratrace elemental analysis, as a stand-alone methodology for enhancing sample introduction efficiency, when physically paired with other vapor generation approaches^{121, 182}, or when combined with conventional solution sample introduction.^{183, 184}

The simplicity and compact nature of the needed apparatus, especially when UV photodiodes are available, make for a potential field instrument when combined with a myriad of low power mini-plasma platforms.^{127, 185}

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Table 1. Vapor generation: advantages and disadvantages.

<u>/ advantages</u>	<u>disadvantages</u>
enhanced analyte introduction efficiency	expensive, unstable chemical reductants
enhanced analyte flux to source	interferences from (transition) metals
matrix separation	pH effects
high selectivity	limited applicability
reduced interferences	limited concentration range
enhanced sensitivity and LODs	non-uniform response from different species
can be hyphenated with chromatographies	requires separate chemfold
direct speciation possible	waste generation
effective for pre-concentration	
ease of automation / use with many detection systems	
analyte coverage is expanding	
remains an exciting field of research	

Table 2. Advantages and disadvantages of PVG

<u>features / advantages</u>	<u>disadvantages</u>
“green” chemistry	interferences from oxidants
eliminates need for fresh chemical reductant	
simplifies flow injection manifolds	
less violent reduction process for GLS	
reduced H ₂ generation - compatible with low power plasma sources	
reduced interferences from concomitant elements	
high efficiency for product generation	
enhanced LODs	
provides for direct speciation scenarios	
broad scope of elemental coverage	

Table 3. Dominant products of photochemical vapor generation.

analyte	Generation medium			reference
	formic	acetic	propionic	
Hg(II)	Hg ⁰	Hg ⁰	Hg ⁰	70, 71
CH ₃ HgCl	Hg ⁰	Hg ⁰	Hg ⁰	70, 71
Se(IV)	SeH ₂ /SeCO	Se(CH ₃) ₂	Se(C ₂ H ₅) ₂	30, 51
Se(VI)	NR (TiO ₂)	NR (TiO ₂)	NR (TiO ₂)	30, 51
As(III/V)	AsH ₃	As(CH ₃) ₃	As(C ₂ H ₅) ₃	72, 73
I(-I)	HI	CH ₃ I	C ₂ H ₅ I	74
Br(-I)	HBr	CH ₃ Br	C ₂ H ₅ Br	75
Ni(II)	Ni(CO) ₄	Ni(CO) ₄	--	76
Fe(II/III)	Fe(CO) ₅	Fe(CO) ₅	--	77
Co(II)	Co(CO) ₄ H ₂	--	--	78

NR: no reaction, --: not determined

Identification by direct injection GC-MS or cryotrapping/GC-MS

Dominant radicals present: formic: ([•]H, CO); acetic ([•]CH₃, CO); propionic: ([•]C₂H₅, CO)

Table 4. PVG generation media and estimated derivatization yields.

element	medium	~ ϵ , %	reference
As(III)	acetic	75	72
Sb(III)	acetic/formic	30	63
Se(IV)	acetic	50 (61)	29 (57)
Fe(II)/Fe(III)	formic	60	81
Co(II)	formic	42 (25)	49 (82)
Cd(II)	acetic	95	83
Ni(II)	formic	35 (100@60° C)	66
Hg(II)	formic	95	84
Pb(II)	formic	44	65
I(-I)	acetic	94	74
Br(-I)	acetic	95	75
Os(VIII)	water	96	67

FIGURES AND CAPTIONS

Figure 1. Schematic of typical PVG system.

Figure 2. Emission spectrum from a low pressure mercury discharge lamp.

Figure 3. Absorption spectra for 5 % (v/v) solutions of (A) formic and (B) acetic acid, showing the 254 nm emission line from a photo source.

Figure 4: LMCT bands for 200 mg/L Fe(III) in pH 2: (A) 30 % formic and (B) 30 % acetic acid.

Figure 5. PVG synthesis of R_2Se *via* radical attack on lone pair of electrons of Se(IV).

Figure 6. Photo-redox reactions catalyzed on the surface of a TiO_2 particle; formic acid serves as the hole scavenger to minimize direct recombination of electrons and holes released from the conduction and valence bands, respectively.

Figure 7. UV-Vis absorption spectrum showing CTTS bands of 200 mg/L I^- in 5% acetic acid against a reference of 5% acetic acid.

Figure 8. Impact of added (A) NO_3^- and (B) NO_2^- on PVG response from 10 ng/mL Se(IV) from 4 % acetic acid.

Figure 9. Solution electrode glow discharge mediated vapor generation system. Reprinted with permission from reference 168. Copyright (2014) American Chemical Society.

Figure 10. Thin-film dielectric barrier discharge plasma-CVG-AFS. Reproduced with permission from reference 176. Copyright (2016) Royal Society of Chemistry, UK.

Figure 1: Implementation of generic PVG system

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Graphical abstract