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Systematic evaluation of advance in application and discharge mechanism of solution electrode glow discharge

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ABSTRACT

As a kind of microplasma sustained in air, solution electrode glow discharge (SEGD) ignited between the liquid electrode and metal electrode is attractive to the fields of optical emission spectrometry and mass spectrometry due to its unique advantages, such as low power consumption and low carrier gas consumption. Moreover, the complex and efficient reactions in the liquid phase and plasma phase of SEG D make it considerable research potential in the fields of biology and medicine, material synthesis, electrochemistry. Considering the close relationship between the various fields on SEG D, here we are devoted to provide an overview of the development of SEG D in various fields. More importantly, a systematic discussion on the discharge mechanism is conducted based on the research process in various fields for getting deeper insight into the SEG D.

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1. Introduction

Various SEG D-based discharges have been explored, including electrolyte-cathode discharge (ELCAD) [1], solution cathode glow discharge (SCGD) [2–8], solution anode glow discharge (SAGD) [9–18], atmospheric pressure glow discharge generated in contact with a flowing liquid cathode/anode (FLC/FLA-APGD) [17], capillary liquid electrode discharge (CLE D) [19], capillary liquid electrode microplasma (CLEP) [20], the electrolyte jet cathode glow discharge, liquid drop anode-atmospheric pressure glow discharge (LDA-APGD) [15], liquid cathode glow discharge (LCGD) [21], single-drop solution electrode glow discharge (SD-SEG D) [22] and so on. Although the above SEG D-based discharge have different discharge structures and naming methods, the discharge is essentially generated in a gap between a conducting liquid and another electrode by applying a high voltage (dc or ac) at atmospheric. SEG Ds referred to as the solution cathode glow discharge (SCGD) and solution anode glow discharge (SAGD), have demonstrated important advantages over conventional plasma sources for liquid analysis, such as inductively coupled plasma (ICP). Studied as radiation sources for optical emission spectrometry (OES) and ionization source for mass spectrometry (MS) and chemical vapor generation (CVG) source for many years [13,23–25], solution-electrode

glow discharges (SEG D), a class of atmospheric-pressure glow discharge where one electrodes is a flowing liquid, have garnered a great deal of interest within the spectrochemistry community. Though initial evaluation of the SEG D sources yielded poor figures of merit compared to the ICP [23,24,26–28], a myriad of efforts have been devoted to bolster analytical performance and expanded applicability. Reduction size of discharge volume and correspondingly increase power density for SEG D [29,30], reversal of the discharge polarity (switching between SCGD and SAGD) [9,10,12,15–17], electrolyte solution modification [4,8,12,14,15,31–43], exploiting the spatial emission structure of plasma [44–46] and coupling with other front-end element separation and pre-enrichment technology have been performed [11,33,35,47–62].

Up to now, the SEG Ds offer certain advantages over other solution-analysis techniques. This type of discharge does not require any compressed gases, unlike most flames (which require fuels and sometimes oxidants) and most other plasmas (which often require a noble gas). The power used with an SEG D is typically ~70 W, which is much less than that commonly used by plasmas suitable for solution analysis, such as inductively coupled plasma (1–1.5 kW to power the plasma). Moreover, The SEG D radiation source produces relatively few (primarily atomic) analyte emission lines, which guarantees lower requirements for spectral resolution [61,63]. All these traits mean that the instruments based on SEG Ds have a small footprint, which gives SEG Ds potential as portable instruments for the determination of elements or anion and chemical vapor generation [30,64]. To date, the optical emission spectrometry

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try based on SEG D has emerged as a viable analytical tool poised to provide both lab-based as well as field elemental analysis of aqueous sample by simplifying the structure of SEG D [7,30,60,61], using a compact spectrograph [61], battery power [5], automated analysis [5,54], minimizing the matrix effects [33,36,38,39,62,65–67], and reducing sample consumption [4,15,33,52,54,60–62]. The chemical form of element is of interest rather than just the elemental concentration. Since chemical form of elements controls its bioavailability, transport, persistence and impact on the organism and its living environment, emphasis is put also on speciation analysis of elements, which can be performed by means of coupling SEG D with on-line separation techniques [47,50,51,53,60]. Not only limited to radiation source for atomic spectrometric, the SEG D is a highly versatile ion source capable of providing both elemental and molecular mass-spectral information. A variety of ions, ranging from bare elemental ions and adducts to intact organic and inorganic molecules, produced by SCGD demonstrate the utility and potential impact of the SCGD in the area of mass spectrometry [68,69].

As mentioned above, significant efforts have been devoted to developing novel source and sampling techniques for analytical atomic spectrometry and mass spectrometry based on SEG Ds. However, almost most these developments have taken place in only a handful of laboratories, and like the other designs, general acceptance has not been achieved, at least as measured by the lack of availability of commercial instrumentation. The key factor restricting the commercial application of SEG Ds is that a definitive mechanism for SEG Ds cannot be offered at this stage of study, which includes the atomization, excitation, ionization of elements and molecular fragmentation.

This review surveys the development of SEG Ds, including its use as radiation source, ion source and chemical vapor generation in the past years. Furthermore, a systematic discussion is carried out on the mechanism research for SCGD and SAGD. Our personal view of some current research results is highlighted in the following and the future development trends of SEG Ds are proposed based on the existing research.

2. Design trend of SEG D

2.1. SCGD

The phenomenon of discharge between metal electrodes and electrolytes was first discovered in the process of Cubkin's studying chemical experiments in 1887. Subsequently, Cubkin named the discharge as an glow discharge electrolysis (GDE) [23]. Since then, atomic emission lines characteristic of copper and indium (which were present in the cathode electrolyte) were observed from the plasma in a GDE-type setup [24]. Shortly thereafter, a new phenomenon closely similar to those produced by passing a discharge to the surface of the solution at reduced pressure, termed "contact glow-discharge electrolysis" (CGDE) was found [70,71].

The first hint that atomic emission was observed from glow discharge laid a foundation for the subsequent emission studies glow discharge. Then a new modified glow discharge electrolysis setup was provided by Cserfalvi *et al.* [26] and the glow discharge (GD) was first applied to quantitative analysis by using a monochromator to collect the spectra. Cserfalvi *et al.* later called modified design electrolyte-cathode discharge (ELCAD) which had evolved since that time in response to several studies and this was the first discussion on the analytical characteristics of ELCAD [27,28]. In order to refine the mechanism research, a modified ELCAD which allowed to vary the air pressure in the ELCAD system was proposed [72]. Based on the previous related basic research, Park *et al.* [63], and Kim *et al.* [73], respectively, using closed ELCAD [70] and open-air type ELCAD [27], developed and studied for fundamental

and analytical applications for determination of trace heavy metals in water. Since then, a further modified the ELCAD cell was used for determination of most concerned toxic heavy metals, *e.g.*, Hg and Cd, by introducing an open-air channel [74]. Since the application in the detector field was not allowed, a correctly designed and spatially well stabilized capillary cathode discharge source which runs with an electrolyte flow rate above the total evaporation point was presented [75]. A further simplified ELCAD design, which they termed solution-cathode glow discharge (SCGD), was proposed by Webb [1,44]. These above researches based on GDE were doubtless of great significance for later SCGD application and mechanism research. Fig. 1 shows the evolution of SCGD systems.

2.2. SAGD

In 1958, the fact that a glow discharge could also be generated between the solution anode and the metal cathode was discovered, which was known as SAGD [24]. It should be noted that no emission from the excited atoms of the dissolved metals can be observed in the early stage [26]. Since then, the SAGD has not been used as the radiation source for the spectrochemical analysis for a long time and the attention was exclusively focused on the SCGD. At this point, it is worth mentioning that the electrical characteristic and the spectroscopic parameters of the SAGD proposed in this period were studied [76–79]. Furthermore, the ability of SAGD to initiate and control electrochemical reactions at the plasma liquid interface opens a new direction for electrochemistry, which highlights the critical role of SAGD in the reduction of target constituents in electrolyte [18,80–82]. Since then, the developed SAGD as a radiation source for optical emission spectrometry (OES) was proposed for the highly sensitive determination of Cd and Zn [16]. Moreover, further researches deepened this topic and extended the application of the SAGD, which was equipped with cooling block, for other elements, *e.g.*, Ag, Cd, Hg, Pb, Tl, In and Zn [9,12,17]. The design of using titanium rod as the discharge electrode of SAGD system can also ignite and maintain stable plasma, which provides a certain basis for further simplifying the structure of SAGD [10]. Another configuration of the SAGD-OES was described by Jamroz *et al.*, who further modified the design of the discharge cell by placing a liquid sample drop on a graphite disk anode and significantly reduced the consumption of samples [15]. Not only limited to the radiation source for OES, another application of the SAGD was generation of chemical vapor, which was much higher than the conventional electrochemical hydride generation with no requirement for other reducing reagents [13].

3. Analytical performance and applications

As mentioned above, various versions of SEG D systems was developed as radiation source, ionization source, plasma-assisted electrochemistry and chemical vapor generation, which can achieve corresponding functions in different application fields, including quantitative determination and speciation analysis of elements, providing molecular mass-spectral information, efficient generation of chemical vapor, electrolyte metal reduction and so on.

3.1. Radiation source for optical emission spectrometry

The emission lines of the dissolved metals in electrolyte demonstrates the possibility to develop a device for the direct analysis of liquid sample at atmospheric pressures, when using the SEG D radiation source with detection by optical emission spectroscopy (OES) [63,83]. Moreover, from the initial proposal that SEG D has the potential to develop into the portable instruments,

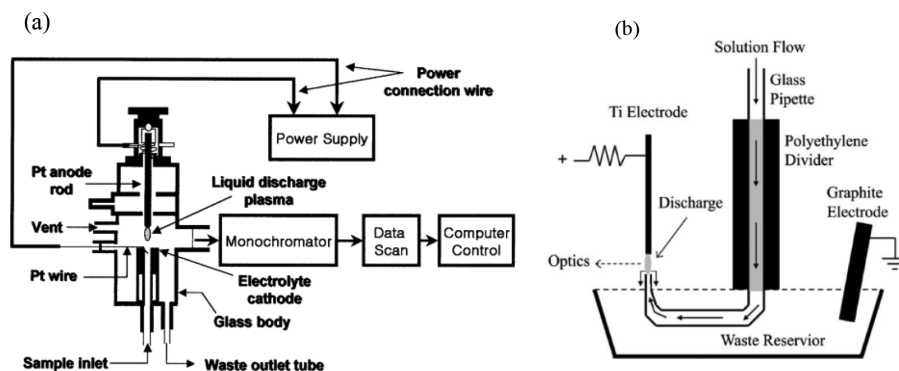


Fig. 1. The structure diagram of (a) ELCAD [74] and (b) SCGD [44]. (a) Copied with permission [74]. Copyright 2001, Elsevier. (b) Copied with permission [44]. Copyright 2005, Royal Society of Chemistry.

to the current battery-operated portable element detection instrument based on SCGD-OES, which shows that the SEGDS seem to be particularly promising for developing as radiation source [5,30,54,60,61,64,84–86].

3.1.1. Design optimization of SEG D radiation source

The related researches carried out on SEG D in the early days mainly focused on the structural design of SEG D, which was found to be an effective method to improve the performance of SEG D-OES [4,5,9,12,15–17,29,30,38,39,43,54,60,61,65,67,79,84,87,88]. Compared with SAG D, significant attention was focused on the SCGD as the spectral radiation sources. In early research, significant efforts were devoted to reduce size of discharge volume and correspondingly increase power density for the SCGD radiation source [29,30,60]. A simplified version of the SCGD with a cathode surface area approximately one-fifth that of the previous version was developed by delivering sample solution through a glass tube (0.38 mm i.d. $\times$ 1.1 mm o.d.) that has been bent into a J-shape [30]. This modification allowed a lower discharge volume (nearly 5-fold, to 2 mm³) and a correspondingly higher power density, which allowed a lower detection limits for a range of metals [30]. Another key parameter of SCGD radiation source is the stability of the plasma. A pulse damping design consisting of a knotted (specifically, a chain sinnet, also known as a daisy chain) length of peristaltic pump tubing was included between the peristaltic pump and the SCGD, which can effectively reduce the plasma instability of the SCGD source induced by the peristaltic pump [30,54,60,61]. A modified pulsation damper consisting of several glass balls, a foodgrade silicone hose and hose connectors was designed and optimized to further eliminate the plasma instability [87]. Besides, a V-groove with a width equal to the i.d. of the electrolyte capillary was cut from the center to the edge on the top of the electrolyte capillary, which was made to enable the solution to smoothly flow down and a stable plasma could be obtained even at a low flow rate of 0.8 mL/min [38,39,43,67,88]. Wang *et al.* also modified the SCGD system to improve its portability by directly connecting a micropipette to the graphite rod to remove the influence of the solution level [65]. Also, Some newly designed SCGDs allowed very low sample consumption [5,84] and further simplified SCGD [4,65], which effectively promoted the development of portable instruments based on SCGD-OES. More recently, a battery-operated portable high-throughput instrument with SCGD-OES emerged by incorporating the sample introduction system, the SCGD radiation system, and the detection system into a small, highly integrated instrument. The corresponding software was written for controlling the instrument on the computer and realizing automated sample detection and data analysis [5].

The research of SAG D designed as spectral radiation source is relatively later. A recent design of SAG D, in which tap water con-

tained in a petri dish that connected to a water reservoir to keep the position of the water surface in good approximation constant during a measurement was used as the liquid electrode, was developed for the measurements of the spatially resolved absolute OH densities and gas temperatures in the SAG D generated in ambient air [79]. Not only limited to the detection of the emission band of OH, a further modified SAG D, which was in the form of a closed U-tube composed of a cathodic cell and an anodic cell, was developed for the highly sensitive determination of Cd, Zn in electrolyte solution used as the anode. The separate discharge cell prevented oxygen from the anode migrating to the cathode and allowed the plasma was maintained in atmospheric pressure argon [16]. Despite the highly sensitive determination of Cd, Zn with SAG D-OES, this topic was deepened by developing a simplified SAG D operated in ambient air with a water cooling block, which extended the lifetime of the electrode and improved the stability of SAG D and further expanded the range of analyzable elements, including Ag, Hg, Pb and Tl [17]. Furthermore, a water cooling block was replaced with a brass heatsink that further simplified design of the system and completely eliminated water consumption [9,12]. Since above research demonstrated the potential of SAG D for radiation sources, a nonflow-through and very straightforward portable SAG D system with liquid drop anode placed on a graphite disk was developed for reliable determination of traces of Cd in small volume samples without cooling block [15].

3.1.2. Modification of liquid electrode composition

Modifying the composition of electrolyte solution serving as liquid electrode is a simple and effective way to improve performance of SEG D, which is mainly achieved by directly adding low molecular weight organic compounds, ionic and non-ionic surfactants to the liquid electrode.

Addition of low molecular weight organic compounds: The main composition of the electrolyte was a key parameter that was regarded to influence the performance of the SEG D system. For SCGD, it has been found that using acids as the supporting electrolyte resulted in greater emission than using salts and that there was variation according to the acid anion [89]. Considering the high element emission and high chemical compatibility, HNO₃ was generally used as the electrolyte of SCGD [4,31]. Besides, a simple but potentially useful way to further lower the detection limits of several metals in electrolyte is treating the supporting electrolyte with low molecular weight organic substances (LMW), e.g. formic acid, methanol, acetic acid and ethanol [4,33,39,42,43]. Especially for some samples with severe matrix interference, such as zirconium and high salinity brines, the determination of trace level of the elements in zirconium alloy was carried out directly without separating matrix by adding formic acid to HNO₃ electrolyte of SCGD and the interference of anions such as SO₄²⁻ in brines can be

effectively eliminated by adding LMW organic substances such as formic acid, glycerol and ascorbic acid [33,39]. It should be noted that different LMW organic substances had different sensitizing effects on elements [4,8,33,39,42,43]. Even if the same LMW organic substance was added to the supporting electrolyte, the sensitization effect on the same element may be different due to differences in experimental parameters such as acid concentration, flow rate, and LMW content [8,42,43].

A research in an attempt to further elucidate the processes involved in the SCGD plasma with LMW organic substances was carried out by measuring and comparing the sample property (conductivity, pH, and density), electrical and spectroscopic property of SCGD. The results did not point to a simple picture of SCGD's operation with organic additives in the sample solution. It has been established that the multiple processes may contribute to improvement of the responses of the elements, which presumably involved evaporation of the solution (no contribution to the analytes signals), formation of the solution droplets (contribution to the analytes signal being enhanced or worsened by LMW organic compounds through size and/or the number of droplets) and volatile species generation and their volatilization from the droplets (contribution to the analytes signals likely through the reactions with the organic compounds and/or their degradation products). The detailed mechanism of interference using low weight molecular organics deserves further investigation [64].

Most recently, the addition of such LMW organic substances to the electrolyte of SAGD also resulted in an improvement in analytical performance of SAGD-OES, including enhancement of emission intensity, improvement of signal-to-background ratio, reduction of the level and fluctuations of the background [12,14,15]. However, the beneficial effect of LMW organic substances was restricted only to electrolyte with specific pH to a certain degree. As recently reported, the intensity of Cd I at 228.8 nm in pH 1 HNO₃ system with a methanol concentration of 1% was higher by 2.1-fold than that achieved without methanol, and the emission from Cd I at 228.8 nm would be suppressed in pH 6 HNO₃ system with a methanol concentration of 1% [14,15]. It should be mentioned here that unlike Ag, Cd, Hg, Pb, Tl and Zn, most of the LMW organic substances, particularly methanol and ethanol, brought a significant enhancement of the emission of indium (In) in SAGD-OES system [12]. Although the LMW organic reagent suppressed the emission intensity of Cd, Pb and Ag in certain parameters, it was assessed that the level and fluctuations of the background in the vicinity of the analytical lines of Ag, Cd, and Pb were lower accordingly, which led to an improvement of the signal-to-background ratio and a lower detection limit for Cd, Pb and Ag determination with SAGD-OES [14].

These findings pointed out a completely different mechanism of the analytes transport into the discharge operated with the liquid cathode and anode. Besides, since a significant intensity improvement resulting from the use of LMW organic substances was observed only for In, it was concluded that it could not be assigned to changes in physical properties of the FLA solution, e.g., through a decrease in surface tension, viscosity or boiling point. More likely, it was rather caused by changes in the course of some electrochemical reactions [12].

Addition of surfactants: A similar sensitization effect for elements determination was also achieved by adding nonionic (Triton X-45, Triton X-100, Triton X-405, Triton X-114, Triton X-705) [36,38,40,41] or ionic surfactants (cetyltrimethylammonium chloride, CTAC) [32,34,37] to the liquid cathode of SCGD system. Besides, the aforementioned surfactants present in liquid cathode led to a substantial reduction of the intensity of molecular bands and the overall background level in addition to the magnitude of its fluctuations, which was not obvious in the addition of LMW organic substances and showed that the mechanism of action of

LMW organic substances and surfactants was not entirely the same [36,42]. The magnitude of the intensity amplification was established to depend on the concentration of the surfactant and its size. Since heavier nonionic surfactants, e.g., Triton X-405 or Triton X-705, were likely to increase the viscosity of electrolyte solutions to a greater extent than lighter nonionic surfactants, changes in the intensity of different species (decreases for molecular bands or increases for atomic lines of metals) observed in the emission spectrum of the discharge were clearly greater for the former surfactants [40,41]. Although somewhat higher amplification factors of the net intensity were obtained for Triton X-705, the handling of standard solutions containing this surfactant was in a long run uncomfortable due to their high viscosity and difficulties in a smooth drainage of the cathode compartment [41]. Another method was developed to significantly improve the sensitivity of the SCGD-OES system for element determination using a combination of a surfactant (Triton X-114) and potassium iodide, which achieved the maximum enhancement for thallium determination compared with other elements (Cd, Hg, Cr, Pb) [40].

The addition of ionic surfactants, namely cetyltrimethylammonium chloride (CTAC), to the liquid cathode of SCGD also resulted in the enhanced sensitivity of SCGD-OES toward Cd, Hg, Pb and Cr while decreasing the background intensity and fluctuation of atomic emission lines of above elements [37]. However, it should be noted that with the introduction of the analytes through the flow gas jet nozzle anode of SCGD system, the presence of the non-ionic surfactant results in deterioration of elemental emission intensity, which showed that the benefits associated with the addition of the surfactant to the liquid cathode solution in the conventional SCGD were primarily related to the improvement of the metals ions transport from the liquid cathode to the discharge zones [35].

Compared with the SCGD system, the discharge of SAGD system with addition of the nonionic surfactant (Triton X-405 at 0.5% m/v) to the liquid anode was very unstable, probably due to a sudden change in surface tension and viscosity of the drop. Thus, this aiding substance was neglected for the SAGD-OES system [15].

3.1.3. Modification of discharge gas atmosphere

A less frequent modification is the change of the composition of the discharge gas atmosphere, which can be performed by replacing a conventional metallic pin electrode with a miniature flow of supporting gas from a nozzle anode/cathode [9,90–93], or by inputting supporting gas to discharge chamber with non-electrode hollow channel [16,18,89]. Both of the two gas introduction methods can ensure that the carrier gas effectively participates in the plasma gas phase reaction with a considerable impact on stabilizing the discharge, modifying plasma composition and offering much better excitation conditions for SEG [9,89,90,93]. It should be noted that the influence of the supporting gas in SEG on the emission spectrum and discharge stability is restricted by many factors, including carrier gas composition, sampling method of analyte, liquid electrode structure. The carrier gas composition refers to the composition of the gas atmosphere in discharge and depends on the discharge chamber construction and the type of supporting gas provided. For the fully open-to-air discharge chambers, air is always involved in the discharge even if a certain supporting gas (e.g., CO₂ [90], Ar [18,90,93], He [90,93] Cl₂ [89], H₂-Ar [48,51,53], H₂-He [47,58], O₂ [18], N₂ [18]). The sensitivities of the individual atomic emission lines of alkali metals in the open-to-air systems working with different microjet-supporting gases (Ar, He, CO₂) were comparable to each other. Compared with this fully open-to-air discharge chambers, operating SCGD in the semi-closed system with a certain supporting gas (CO₂, Ar or He) caused a several-fold (from 1.5 to even 4) drop in the intensity of the analytes atomic emission and a significant decrease the spectral inter-

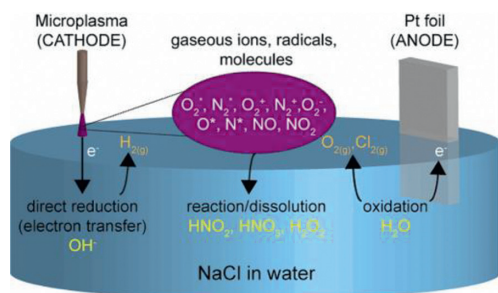


Fig. 2. Potential reaction paths occurring in a plasma-liquid system with an aqueous solution of NaCl. Reproduced with permission [18]. Copyright 2013, American Chemical Society.

ferences (especially those from the NO molecular bands), which is a natural consequence of the air supply cut-off [90,93]. As shown in Fig. 2, even though the products (NO, NO₂, etc.) forming in discharge phase subsequently dissolve into liquid phase and eventually change the liquid phase composition [18,94], the discharge system with a flowing liquid electrode structure avoids the influence of the above-mentioned dissolution process on the spectral emission by continuously updating the liquid in contact with the plasma. On the other hand, the sampling method in which the analyte is converted into volatiles and introduced into the discharge phase from the anode nozzle rather than the liquid phase can change the influence of the discharge atmosphere on element emission [35,48,50,57,58].

3.1.4. Modification of sampling method

In general, most routine determination of elements in liquid samples can be accomplished by SEG-D-OES system of which sampling methods were in a continuous flow mode. However, faced with the challenge of accurately determining elements in complex matrices, a sampling technology of coupling element separation and preconcentration technologies with SEG-D have emerged. A flow injection (FI) sampling method to decrease the load of the discharge with potentially interfering components of the samples solutions was coupled with SCGD system [1,33,42,43,49,54–56,60–62,84]. This flow injection sampling system needed to be implemented by means of standard six port valves along with sample loops, which simultaneously allowed high throughput sampling with small sample volume and was particularly well suited to transient analysis [42,43,60–62,64,95]. Further improvement of sample throughput for SCGD-OES was achieved by performing automated, on-line generation of calibration curves and standard-additions plots, which also minimized the time required for off-line sample preparation. The first method employed a gradient high-performance liquid chromatography pump to perform on-line mixing and delivery of a stock standard, sample solution, and diluent to achieve a desired solution composition. An alternative method employed a simpler system of three peristaltic pumps to perform the same function of on-line solution mixing [54].

Driven by the need of sensitive determination of different elements in complex matrices, a method to improve determination sensitivity for element was developed by coupling SCGD-OES with FI based on-line solidphase extraction (SPE) and variants of extraction materials packed in SPE microcolumn for efficient separation and preconcentration of the target elements were synthesized, including L-cysteine-modified mesoporous silica for Hg(II) [56], lysine-modified mesoporous silica for Cr(VI) [55], mesoporous silica-grafted graphene oxide for Pb(II) [49]. To simplify such FI-SPE system, the effluent from the on-line solid-phase extraction system was directed into the sample capillary of SCGD.

Another opportunity to broaden the way of analytes' delivery to the discharge and significantly improve the determination sensitivity of SCGD-OES system was opened by applying the miniature flow gas jet nozzle anode. This design allowed the direct introduction of volatile analyte into SCGD from anode and provided feasibility for coupling SCGD with vapor generator, e.g., as cold vapor of Hg, As, Se, Pb, Ge, Sn and Sb formed in the cold vapor generation (CVG) and purged from a reaction/separation system by a stream of He carrier/jet-supporting gas [48,51,53,57,58]. Moreover, photochemical vapor generation (PVG), as a promising technique for the generation of volatile species, was demonstrated to be less toxic, simpler, and subject to little interference from transition metals, which was successfully coupled to SCGD-OES for the highly sensitive determination of Hg. The selective vapor generation characteristics of PVG to element valence states under different PVG parameters provides important technical support for applying PVG to element valence state analysis, e.g., Hg [50]. Hydride generation (HG), as a kind of CVG technology, also has the characteristics of selective vapor generation for element valence (Sb, As, Se, etc.) valence states, which provides feasibility for elements valence analysis carried out by coupling SCGD with HG system [47,51,53]. The resultant analytes-containing dry aerosol produced by ultrasonic nebulization (USN) can also be transmitted to SCGD system through the gas nozzle jet anode and the sensitivity of SCGD-OES was improved about one order of magnitude, which proved the validity of such coupling SCGD with USN sampling technology [35].

The design of the miniature flow gas jet nozzle electrode is also attractive to improve the performance of SAGD system. The direct introduction of volatile analyte into SAGD from cathode can be performed by coupling SAGD with vapor generator based on the design of the miniature flow gas jet nozzle cathode, which improved the determination sensitivity for elements (Hg, Pb, As, Bi, Sb and Se) and the susceptibility of SAGD to the matrix-induced interferences [11,96,97].

The anions in sample are of interest rather than just the metal cation. By coupling a high performance liquid chromatograph (HPLC) along with an ion suppressor (IS) and a replacement column (RC) miniature to a SCGD system, a new method named SCGD-replacement-ion chromatography (SCGD-RIC) was developed to measuring the anions, including F⁻, Cl⁻, Br⁻, BrO₃⁻, NO₃⁻, CH₃COO⁻, SO₄²⁻ and SO₃²⁻. By tracing the Li signal in SCGD, the mentioned anions can be indirectly determined. Most importantly, due to the exceptional sensitivity of SCGD for alkali metal species [60], the above system has the potential to be highly sensitive for IC detection [59].

A novel capillary microplasma analytical system (C-μPAS) system was constructed through a interface-free mode to integrate capillary electrophoresis (CE) with SAGD-like discharge by sharing one single d.c. power supply and can also perform the determination of anions (Cl⁻, Br⁻, CH₃COOCl⁻, CH₃COOBr⁻) in sample [52]. The C-μPAS integrated sample introduction, analyte species separation and analytical signal detection into one compact unit, which mainly depended on the discovery that a CE process can be induced by starting a SEG-D-like discharge. Furthermore, the reverse C-μPAS formed through exchanging the cathode and anode also allowed the determination of metal cation [52].

A drawback of coupling SEG-D with vapor generation is that it reduces the ability of the atomization/excitation source to act as a multi-elemental detector. Not all elements are amenable to vapor generation, and those that are sometimes require different conditions from each other.

3.1.5. Radiation acquisition optimization

The physical structure of the SCGD shown in Fig. 3 includes the negative-glow (region of intense emission that ranges from

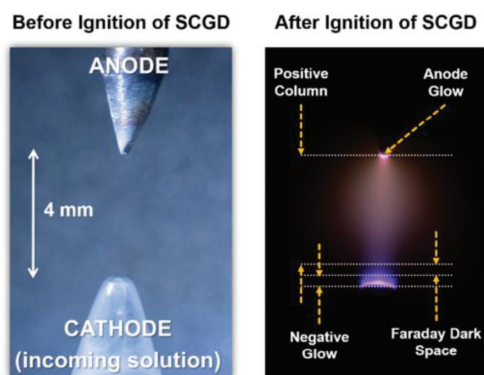


Fig. 3. Photographs of the SCGD before and after ignition on a solution of 100 mg/L indium in 0.1 mol/L HNO_3 . Note the presence of the characteristic glow-discharge emission regions. Copied with permission [45]. Copyright 2016, Elsevier.

the cathode surface to ~0.5 mm above the cathode), Faraday dark space (~0.5 mm tall region above the negative glow), positive column (~3 mm tall region above the Faraday dark space) and anode glow (region of strong emission at the anode surface) [45]. It has been revealed that elemental and molecular emissions are not spatially homogenous throughout the SCGD, but rather conform to specific region of the discharge [1,44–46]. A more systematic evaluation for the SCGD on a per-element basis was performed by collecting vertical profiles of the emission intensity, signal-to-background ratio, and signal-to-noise ratio in SCGD with an optimized spatial filtering [45]. The emission spectrum collected only from regions of the discharge where analyte species emit strongly and background emission (from elemental or molecular sources) is lower hinted that exploiting this inhomogeneity can apply to improve analytical performance and flag or eliminate matrix interferences entirely [44,45]. Considering the spatial distribution difference of emission between elements in SCGD, an individually optimized spatial selection is essential for SCGD-OES to ensure the analysis performance for different elements. However, because the method utilizes spatial windows individually optimized for each element, and it is limited in application to spectrometers equipped with two-dimensional detector arrays (charge coupled device (CCD), electron-Multiplying CCD (EMCCD), etc.) or instruments capable of scanning an image across the entrance slit of a spectrometer. By exploiting a single, compromise spatial window, spatial filtering can be effectively applied to instruments without a two-dimensional detector array and provided similar results for most elements [45].

3.2. Induce vapor generation

An interesting application outside elemental analysis has been demonstrated in which the SEGDC systems were used as a novel cold vapor generation for inductively coupled plasma optical emission spectrometry (ICP-OES) [25,98–100], atomic fluorescence spectrometry (AFS) [13,101] and laser-induced breakdown spectroscopy (LIBS) [102].

A closed SCGD system with a U-tube design was first employed to replace the nebulizer unit of ICP-OES and compared with the standard pneumatic nebulizer in an ICP-OES analyzer to investigate the glow discharge sputtering process of SCGD, which showed the potential of SCGD applications as vapor generation technology [98]. Compared with this SCGD system with an U-tube design, a more compact SCGD (gas-phase internal volume of about 3 mL) with lower dead volume and limits dispersion was developed for the initial experiments to investigate its feasibility as a

vapor-generation method for mercury, iodine and osmium [25,98–101].

It was found that not only inorganic mercury (Hg(II)) but also organic mercury (thiomersal) can be directly transformed to volatile Hg vapor in a high vapor-generation efficiency and an extremely rapid speed without prior oxidation. Furthermore, compared to other CVG methods, interferences from concomitant ions were mild [25]. Most importantly, since the decomposition of organic mercury species and the reduction of Hg^{2+} was instantaneous and could be completed in one step with this proposed SCGD induced vapor generation system, it was developed as interface to on-line couple high-performance liquid chromatography (HPLC) with atomic fluorescence spectrometry (AFS) for the speciation of inorganic mercury (Hg^{2+}), methyl-mercury (MeHg) and ethyl-mercury (EtHg) [101]. For the vapor generation of iodine, both iodide and iodate could be directly converted to volatile iodine vapor SCGD induced vapor generation system in a high vapor-generation efficiency without prior reduction, and the same was suitable for osmium [99,100].

Another method to further enhance the vapor generation efficiency of elements (Hg(I)) in the SCGD induced vapor generation system was the addition of low molecular weight organic acids (formic or acetic acids) or alcohols (ethanol) in sample [25]. Similar to formic acid, it was found that 2-mercaptoethanol was also effective in enhancing the vapor generation efficiency of Hg in SCGD induced vapor generation system [101]. However, the LMW organic substances (ethanol and acetic acid) increased the vapor generation efficiency of KIO_3 while a reduction in vapor generation efficiency of KI was found, which might be related to differences in the vapor generation mechanism of KI and KIO_3 and also indicated that the presence of LMW organic substances in samples would cause some interference for iodine determination [99].

A high efficiency vapor generation for elements can also be achieved on the basis of solution anode glow discharge. Considering the different mechanisms of SAGD and SCGD, the elements that can be converted to vapor in SAGD induced vapor generation system were different from SCGD, e.g., Cd and Zn for SAGD system. Besides, it should be mentioned that the generated volatile Cd and Zn species were both in molecular form [13].

3.3. Ionization source for mass spectrometry

The SCGD, as a novel ionization source for mass spectrometry, enabled ionization of elements and controlled, tunable fragmentation of peptides at atmospheric pressure, which opened up the possibility of SCGD as a highly versatile ion source capable of providing both elemental and molecular mass-spectral information [68,69]. Also, samples introduced as solids and gases were readily ionized by the SCGD, suggesting the source has applications in ambient ionization [68].

The elemental mass-spectral information produced by SCGD was composed of bare elemental ions and a variety of elemental ions bound with one or more adducts that was commonly the addition of one or more water molecules, which suggested that interpretation of elemental mass spectra could be difficult on low-resolution mass analyzers. Despite the large number of adducts formed for most elements, which result in dispersion of the signal across many m/z channels, detection limits for SCGD-MS remained at levels useful for trace determination of elements (Cu, Cd, Cs, Pb, and U). However, the precision values for elements determination with SCGD-MS were comparatively poorer than those obtained with SCGD-OES, which likely resulted from the low transmission efficiency from SCGD to MS. Besides, some stable complex ions (UO_2^{2+} , CrO_4^{2-} , MnO_4^- , VO_3^+ , etc.) were resistant to dissociation in the SCGD even with in-source collision-induced dissociation (CID), which showed the SCGD source could be used both to

identify the oxidation state and to quantify these species separately from other chemical forms [68].

Another important information provided by SCGD outside elemental mass-spectral was the mass-spectral of biopolymers and small molecular species. The molecular mass spectrometry of SCGD-MS revealed that fragmentation of molecular can be tunable by adjustment of the discharge current [68,69]. The trend of molecular fragmentation with SCGD current (high currents produced extensive fragmentation) for small molecular species was reversed from that for biopolymers, where low currents produced extensive fragmentation and high currents produced intact ions [68,69]. This seemingly counter-intuitive enhanced fragmentation for biopolymers under low-power conditions might be explained by the earlier work by optical emission, which revealed that radical, molecular species were more prevalent in the SCGD at reduced currents [31]. Moreover, the mass spectra for biopolymers in SCGD-MS showed that an electrospray-like ionization process is occurring at high discharge currents (e.g., 70 mA). Most importantly, it was found that the SCGD appeared capable of distinguishing between these two isomeric residues [69]. Above findings hinted that the both the fragmentations of biopolymers and small molecular species can be tunable by adjustment of the discharge current and hinted that the mechanism of fragmentation of small molecular species (such as TEP) was different than that which leads to fragmentation of biopolymers. Furthermore, these results suggested the versatility of the SCGD as an ion source for mass-spectrometric analysis of a wide variety of inorganic and organic analytes. The systematic comparison of SEG D applied to element analysis performance is shown in Table S1 (Supporting information).

3.4. Additional application

While the concentration is focused on the application of SEG D in analytical chemistry, there are some applications where SEG D would be technologically useful. Preliminary results presented in recent research indicated that SCGD system may successfully be applied for the efficient and fast on-line continuous flow chemical degradation of toxic and hazardous organic and inorganic species in wastewater solutions [91]. It should be noted that due to the overflowing liquid cathodes of SCGD, although the contact of discharges with treated solutions was relatively short, the degradation efficiency of pollutants (methyl red dye, Triton X-45 and X-405 non-ionic surfactant and hexavalent Cr ions) was found to be within 50%–100% and strongly depended on the solution flow rate [91].

Apart from the application of SCGD to the degradation of pollutants in wastewater, the ability of SAGD to initiate and control electrochemical reactions at the plasmaliquid interface opens a new direction for electrochemistry based on interactions between gas-phase plasma and solution electrode. For example, the plasma produced by SAGD could serve as the cathodic electrode to reduce H^+ to H_2 . Beside, plasma reduction in SAGD system may offer advantages in materials synthesis, as recently mentioned for antimicrobial silver nanoparticles [103] and colloidal metal nanoparticles [104], as well as silver nanoparticles and deposition of them onto a polymeric substrate, [105] where the absence of a solid electrode could enable homogeneous material synthesis.

The active particles generated during the discharge interact with water molecules to initiate a cascade of chemical reactions and produce a unique mixture of highly biochemically-reactive chemistries generally termed plasma activated water (PAW) [94]. The PAW generated by the atmospheric-pressure plasma in a continuous flow system has been proved to be a promising an effective environmentally benign disinfectant, the activity of which is closely linked to the generation of peroxyxynitrite. The alkaline con-

ditions and low temperature play an active role in prolonging the activity of PAW generated from air atmospheric plasma [94]. The transient activity of PAW, where PAW reverts to water within days of storage and application, suggests that it can become a green alternative to conventional chemical treatment methods, yet the issues of scale up and the not fully understood mechanism of activity remain [94].

Above work highlighted the critical role that SEG D system can play in plasma/liquid interactions with broad implications, including emerging applications in plasma medicine, plasma-liquid materials synthesis and environmentally benign disinfectant [81,91,94,103–105]. A deeper understanding of the fundamental chemical processes that govern the temporal evolution of reactive chemistry in plasma is essential to further optimize the application performance of SEG D.

4. Mechanism research progress

The researches on the mechanisms of elements atomization, excitation, ionization and molecule dissociation or that fragmentation in SEG D systems hinted that the behavior in SEG D is complex [18,45,64,68,69,80,98]. The presentation of a identified and complete mechanism for SEG D, in spite of recent technical developments, remains to be an obstacle for the further development of SEG D.

4.1. Mechanism research for SCGD

Although the analytical performance of the SCGD as a radiation source or ionization source is well characterized, the mechanism through which the discharge atomizes and excites or ionizes analyte from the sample solution remains a point of debate [106]. At present, the mechanism models proposed for SCGD mainly include cathode sputtering model [26,28,98], electrospray-like model [30,31,44,68,69,106], and combination of several mechanisms [64,69,91], but no clear experimental results directly indicate that the discharge process of SCGD is one of the above-mentioned mechanism models. Besides, the present stage of investigation has not yet been able to meet the requirements of the proposal of an exact mechanism for the SCGD-induced fragmentation of peptides and the atomization, excitation or ionization of elements [64,69].

4.1.1. Cathode sputtering model

The cathode sputtering model can be divided into three models according to its sputtering particles, namely ion sputtering through direct ion–ion collision [26,28,98], neutral atom sputtering from the solution [98] and quasi-neutral compound sputtering from the solution [98].

In the assumption of ion sputtering through direct ion–ion collision, the energetic bombing ion coming from the plasma directly hits the metal ion in the solution surface layer of liquid cathode. Since an $\sim 10^7$ V/m electric field existed in cathode dark space (CDS) layer which generated a strong pushing force on positively charged particles and returned them towards the cathode, these positive ions, however, were unable to cross the cathode dark space [28,98]. Hence, a possible mechanisms of recombination, namely a three-body collision process ($M^+ + e + X \rightarrow M + X$), in which the positive ions (M^+) were recombined into neutral particles by electrons (e) with a suitably low energy and X a third body (this may be a neutral atom or an electron) absorbed the energy released during recombination, and then the neutral particles diffused into the discharge region [28]. However, considering the ion size ranges this process had a very low theoretical colliding cross section, hence its role was of the least probability in sputtering process [98].

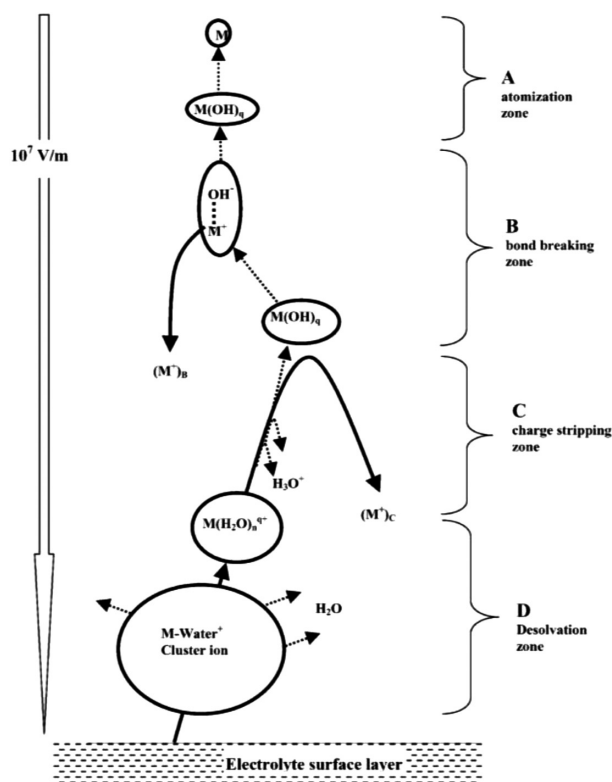


Fig. 4. Schematic diagram of the quasi-neutral compound sputtering model. Copied with permission [98]. Copyright 2005, Royal Society of Chemistry.

Considering the giant repelling field in the CDS region that certainly blocks all positively charged particles to reach the positive column, another assumption, namely neutral atom sputtering from the solution, for sputtering particles of neutral atom was proposed. In this assumption, the electrons produced through the ionization of H_2O molecules by the carrying energetic positive ions from plasma were partly captured by water molecules stabilizing them in the form of H_2O^- (or e_{aq}), namely hydrated electron, which was a very reductive component. Starting with the fact that hydrated electron can produce a detectable amount of neutral metal atoms in metal salt solution, there was a fair possibility of the neutral metal atom production by capturing solvated electrons before its ejecting from the solution and hence, neutral atoms had much more possibility of reaching the plasma through simple diffusion unaffected by the electric field of CDS [101]. However, a very weak correlation of the electron capturing process on the sputtered metal flux was found.

Another mechanism model, namely quasi-neutral compound sputtering from the solution, was proposed (Fig. 4). It was assumed that the primary particles ejected from the surface were charged metal-water complexes or water clusters in the process of cathode sputtering. Above water cluster ions ejected (by the bombarding positive ion collision) from the surface were thermally desolvated; then the resultant hydrate-complex ion started to stabilize by losing hydroxonium ions the strong CDS field. If the kinetic energy received in the ejection step was below a certain level, then the positively charged particle will return to the cathode. Besides, the particles receiving neutral charge through the development of a hydroxyl-compound were further affected by the electric field on the basis of their bond polarizability, which was disrupted by electric field and the naked positive analyte atom fraction returned to the cathode. Only the compounds having stronger OH bonds got into atomization zone, where the atomization took place

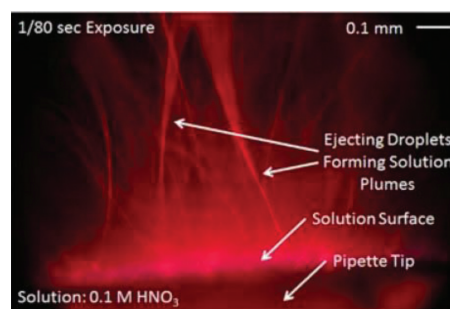


Fig. 5. Laser-scattering images of the SCGD solution-plasma interface. Copied with permission [106]. Copyright 2012, Elsevier.

due to the high gas temperature. Analyte atoms produced in this zone went further up into the excitation region and finally left the plasma as an aerosol. Above mechanism model of cathode sputtering described the element-dependent mass transport process in accordance with the mass spectrometric evidence of gas phase solvated metal ions [98].

4.1.2. Electrospray-like model

Several studies of the SCGD led to the supposition that at least some of the solution was transported into the discharge as droplets, possibly charged and emanating from the rough solution surface in a manner reminiscent of electrospraying [30,31,44,68,69,106,107]. Observations of the SCGD solution-plasma interface by laser-scattering technology showed that the solution surface of SCGD was violently chaotic with a great deal of droplet ejection formation and a plume-like shape of droplet ejection which was similar to the Taylor-cone structure observed with cone-jet electrospray in SCGD, which proposed that an electrospray-like mechanism was responsible for their generation (Fig. 5) [106,108]. Most importantly, the electric field of CDS estimated to be on the order of $\sim 10^7$ V/m [98] or 6×10^6 V/m [77,109] seemed to support that analyte species could be electrosprayed from the solution surface within the SCGD [106]. If the same process similar to electrospray was responsible for removing analyte from the solution phase and introducing it into the SCGD plasma (analyte was most likely carried into the plasma in these droplets), the facts of noticeable decline in the formation of solution aerosol and ejected droplets with the reduction of acid concentration in the solutions can provide a physical explanation for why analyte emission from the SCGD drops as the pH of a solution was increased [106]. Besides, a electrospray-like spectra dominated by singly and doubly protonated molecular ions was observed in the mass-spectral information of renin substrate I produced by SCGD at high discharge currents (e.g., 70 mA). Presence of the doubly charged molecular ion suggests that an electrospray-like ionization process was occurring. However, at the present stage of investigation, proposal of an exact mechanism for the SCGD-induced fragmentation of peptides was premature [68].

4.1.3. Combination of several mechanisms

Another study conducted by comparing the properties of solution before and after exposure to the SCGD plasma and measures how organic additives affect these properties was more biased towards a mechanism model in which a multi-part mechanism was proposed for transporting solution and analyte into the plasma. Evaporation from the cathode surface, droplet generation, and chemical generation of volatile species may each play a role [64].

A general insight of the mechanism for the SCGD-induced fragmentation of peptides was gained by a comparison of the SCGD mass spectra with those obtained by collision-induced dissociation

(CID), electron-capture dissociation (ECD)/electron-transfer dissociation (ETD), photodissociation, thermal dissociation or chemical fragmentation and indicated that the mechanism for the SCGD-induced fragmentation of peptides could also result from a combination of several mechanisms, including the interaction of peptides with gas-phase radicals, ultraviolet radiation generated within the plasma or electrospray-like ionization [69].

4.2. Mechanism research for SAGD

Compared to SCGD, the different discharge behaviors of SAGD for the elements and the different response with the addition of LMW organic substance or surfactants pointed out a completely different mechanism of transporting analytes into the discharge operated with the liquid cathode and anode [12,17]. Moreover, the different electrical and optical emission properties between SCGD and SAGD clearly underlined the significant different behaviors of a liquid anode and a liquid cathode [77,79,109]. In the case of the SAGD, the solution surface was irradiated by the electrons and hence, the dominate process of SCGD in which the metals were transferred to the discharge phase owing to the bombardments of the solution surface with the positive ions was negligible [17]. The release of the analyte from the SAGD liquid to the plasma is related to a unexplained hitherto mechanism, likely including the charge-transfer reactions leading to the formation of their volatile species and the further atomization processes or the spattering of the metals ions and their neutralization by the impact with electrons in the gas phase of the discharge [17].

Certainly, since the concentration of atoms of volatile forming elements (Ag, Cd, Hg, In, Pb, Tl and Zn) in the discharge phase was several times higher as compared to their concentration in the solution of SAGD system, this allowed to conclude that such processes like electrospray formation or solution evaporation did not make a major contribution to transport of these elements in SAGD [9]. Besides, the process of electron-transfer reactions, e.g. the conversion of protons (H^+) to hydrogen gas and the reduction of ferricyanide to ferrocyanide, at the plasma-liquid interface of SAGD system has been proved [80] and hence, it is reasonable to believe that this electron-transfer reactions may also contribute to the formation of volatiles of aforementioned elements [17]. Even though the electron-transfer reactions was indeed confirmed to exist at the plasma-liquid interface of SAGD system, the spatial distribution of the reactions in solution was not clear and it was also possible that some electrons become solvated and reactions occur substantially below the surface [81]. A most recent research directly measured the solvated electrons generated in SAGD-like plasma by their optical absorbance using a total internal reflection geometry and an average penetration depth of the solvated electrons was estimated to be 2.5 ± 1.0 nm, which indicated the distribution of reaction with the solvated electrons in the liquid anode of SAGD [110].

5. Conclusions and future trends

Inexpensive, compact, and capable of using as radiation source, ionization source or chemical vapor generation at atmospheric pressure, the SEG D opens up the feasibility of elements determination, speciation analysis, pre-enrichment of elements, peptide sequencing and providing structural information for molecule by field instruments. Although a series of advances that mainly focused on the application performance of SEG D in the fields of material synthesis, electrochemistry, chemical analysis and so on have been achieved in the last few years, the investigation of microplasma-based techniques is still in its infancy [111]. So far, it is clear that the discharge process in different SEG D systems, including SCGD and SAGD, is different and complicated. Meanwhile,

changing some discharge conditions, e.g., the composition of the atmosphere and the composition of the electrode liquid, will directly affect the discharge behavior of SEG D. However, the detailed mechanisms of these processes in SEG D still cannot be deduced from recent studies, most of which only put forward model hypothesis for SEG D. Hence, it is so promising that further work aimed at understanding the mechanism of transport of analyte to this SEG D source as well as excitation and ionization of analyte in SEG D source is undoubtedly justified, which is clearly needed for further improving the performance of SEG D in several fields.

Declaration of competing interest

The authors declare no conflict of interest.

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