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ORIGINAL RESEARCH ARTICLE

Optimization of oscillated gas-liquid separator for simultaneous heavy metals determination in water sample

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ABSTRACT

A technique has been developed to detect and determine multi heavy metals simultaneously in a water sample. Hydride generating technique was implemented to convert the analyte which present in the water sample (liquid phase) into another form with an improved separation coefficient, called "derivative". This process occurred without changing the original chemical structure. Derivatives were separated from the liquid phase by applying custom made gas-liquid separator (GLS), operated with oscillation. Separated species then transferred into a die-electric barrier discharge (DBD) plasma atomizer where a fragmentation of the analyte into free atoms is occurred. The generated atoms were detected by emission spectroscopy. The presented technique was applied for detection of individual and multi heavy metals simultaneously in water sample and proved useful in terms of reducing the effect of the hydrogen generated, through the process, on suppressing the atoms signal in the DBD atomizer.

Keywords: Gas-Liquid Separation; Heavy Metals Detection and Determination; Species Derivatization, DBD Plasma Atomizer

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1. Introduction

Heavy metals are mostly dangerous to humans and other creatures since they can cause significant effects on the body functions, leading to death in considerable number of cases. Heavy metals content in wastewater discharges is considered the most important reason for contamination of natural water bodies. Hence, and for the sake of controlling wastewater disposal, instant sample analysis is required to detect heavy metals, qualitatively and quantitatively, in their different forms with high resolution. This kind of highly accurate analysis can be achieved by coupling two powerful techniques; the first technique achieves separation of various forms of the element of interest, whilst the second technique conducts determination of the metal to low detection limits.

Methods for heavy metals determination are known of two routines. Changes in the chemical properties of such a media are measured due to interactions from external heavy metal species, in the first routine. The second routine is based on applying spectrometric analysis to monitor changes in species structure upon emerging thermal radiation from different sources (e.g. quartz cell or plasma source).

In our previous work[1], a miniaturized dielectric barrier discharge (DBD) microplasma chip was developed as a radiation source for mercury determination in water samples based on $SnCl_2$ as a derivatizing agent. Same system was used in this research applying sodium and potassium hydroborates as derivatizing agents for single and multi heavy metals simultaneously.

In theory, the efficiency of the hydride generation process (E_{HG}) is represented by the fraction of analyte transported in the form of hydride to the atomizer, as represented by the following formula[2]:

$$E_{HG} = \frac{N_0}{c_0 V_s} \tag{1}$$

Where:

N_0: total number of analyte atoms supplied in the form of hydride to the atomizer;

c_0: analyte concentration in the sample;

V_s: volume of the sample.

Alternatively, the efficiency can be defined for each individual step as follows:

$$E_r = \frac{N_{released}}{c_0 V_s} \tag{2}$$

E_r: hydride release efficiency;

$N_{released}$: total number of analyte atoms released from the liquid sample in the form of hydride.

$$E_t = \frac{N_0}{N_{released}} \tag{3}$$

E_t: hydride transport efficiency, which represents the fraction of the released hydride that would transport to the atomizer.

Thus, individual stages efficiencies are related by the following formula:

$$E_{HG} = E_t \times E_r \tag{4}$$

Accordingly, any disruption that could occur in any of the two stages might lead to disturbing the recorded signal.

Typically, the purge gas (e.g. Argon) is applied to strip the hydride out of the sample solution as well as transporting the released hydride to the atomizer.

Derivatization of the examined analytes has been conducted in this study by applying the hydride generation technique, which is a reaction between the acidified water sample (contains the examined analytes) and the reducing agent (sodium tetrehydroborate, $NaBH_4$). In addition to the generated hydrides, a huge quantity of hydrogen gas is also generated as a result of $NaBH_4$ decomposition. Stoichiometrically, four moles of the hydrogen gas are produced upon decomposing one mole of sodium tetrahydroborate, as illustrated by the following reaction formula[3]:

$$BH_4^- + 3H_2O + H^+ \rightarrow H_3BO_3 + 4H_2$$

It should be noted that the generated hydrogen gas gives rise to the formation of aerosol in the gas liquid separator which consequently disturbs the system performance.

Although the generated hydrogen is considered advantageous for plasma reaction into such extent, it was reported in literature and observed experimentally in this study that a presence of extra hydrogen gas in a DBD plasma reactor affect the plasma stability and result in extinguishing the plasma in some severe cases as illustrated in **Figure 1**, which shows a comparison between the recorded signals in the beginning of the HG reaction and after 2 minutes duration due to hydrogen effect. In this experiment, mercury vapour generation was conducted by using 0.5% m/v $NaBH_4$ stabilized in 0.14% m/v NaOH as a reducing agent. 100 µg/L mercury solution acidified with (1% v/v) HcL was injected to the system with aid of argon gas as a carrier.

Due to its lighter weight, the probability of hydrogen molecule transfer to the atomizer is larger than the generated hydrides, which consequently lead to plasma instability. Chaudhary *et al.*[4] observed this behaviour in their atmospheric pressure cold plasma generator and reported that extra amount of hydrogen lead to destabilize and completely extinguish the plasma. They stated a probable reason for the hydrogen effect on plasma is the ability to alter the electron energy and electron energy distribution function; thus, it would change the population of the reactive species in the discharge.

Although the case described in **Figure 1** represents the derivatization reaction of mercury by using low concentration of $NaBH_4$ (only 0.5% m/v); the disturbance occurred to the spectrum is obviously massive. This case becomes more obvious when using higher concentrations of $NaBH_4$ that is required to derivatize other heavy metals individually or simultaneously. According to the results of the current optimization study, the minimum concentration of $NaBH_4$ that is required to implement the detection of seven heavy metals (simultaneously) was found to be 1.5% m/v, which means possibility of higher hydrogen liberation compared with the previous case of mercury.

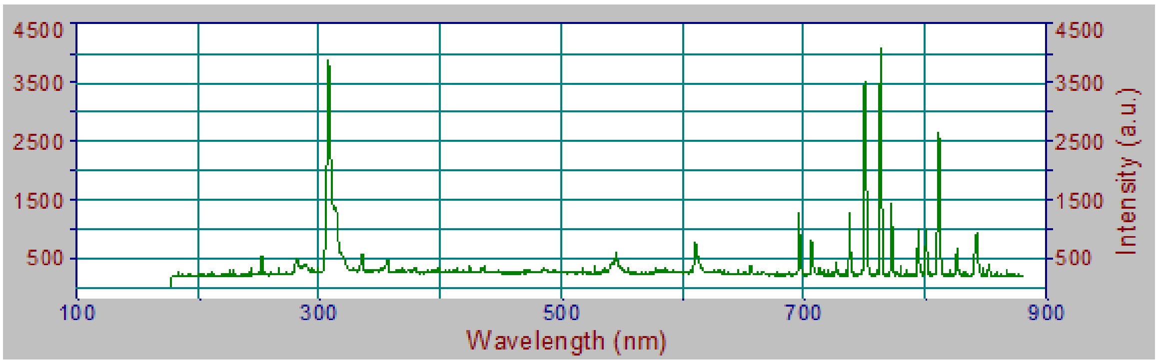


Figure 1. a) Recorded spectrum in the beginning of the reaction.

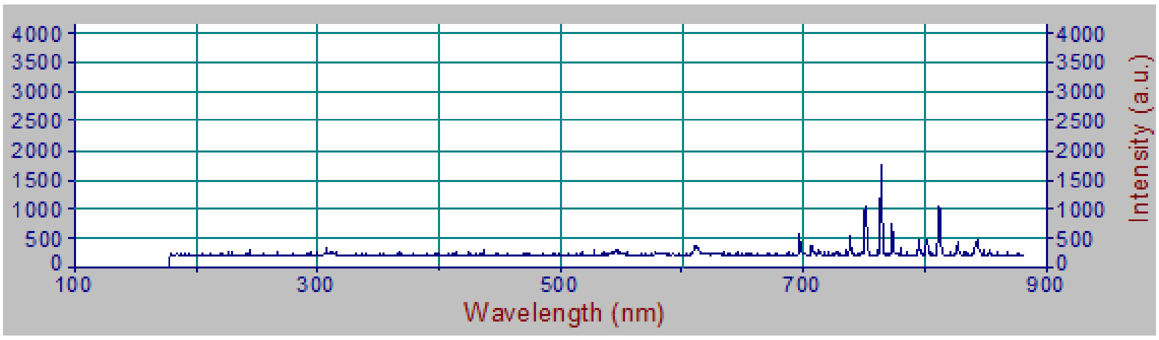


Figure 1. b) Recorded spectrum after 2 minutes.

2. Methodology

A technique based on applying oscillated gas-liquid separator was proposed and examined in this research. The developed system is shown in **Figure 2**. The control strategy of the gas liquid separator has been implemented by assigning a solenoid valve to control the injection of the supporting gas (stream 1) into the GLS (A). The main concept is to supply pulses of the supporting gas through stream (1) which prevents the build-up of high pressure inside the separator and consequently limits the formation of the disturbing factors and facilitates the release of the vapour species without disrupting the bulk. A solenoid valve (Takasago – Japan) with 2 (mm) bore size powered by 12 volt DC was used to implement the injection of the supporting gas pulses. The control strategy of generating the argon gas pulses as well as controlling the other compartments of the proposed system has been accomplished by using a microcontroller (Arduino – Mega) interface which is operated by a PC software. A fibre optic was used to collect the emission spectra which were recorded by (Ocean Optics USB 2000) spectrometer (0.3–1.5 nm FWHM resolution, 600 lines grating density blazed at 300 nm, and 25 µm slit width) and analysed by the Spectra Suite software (Ocean Optics). Other system details are described in our previous paper[1].

In the first instance, several experiments were conducted to investigate the individual detection of single elements. Seven elements were examined individually by applying the continuous gas flow and pulsed gas flow in the GLS includes: Cadmium (288.84 nm), cupper (324.55 nm), tin (326.375 nm), mercury (253.58 nm), arsenic (229.03 nm), nickel (232.06 nm), and lead (220.31 nm). Derivatization of each the elements individually was conducted by applying the optimum reaction conditions which was found applicable for the simultaneous detection of all elements (i.e. acidified water sample (with 1.5 M HCl) contains about 10 ug/L of each examined analyte and using (1.5% m/v) $NaBH_4$ as a reducing agent). The pulsed argon flow experiment was conducted by applying pulses of 75 (mL/min), in a sequence form, for 4 seconds and stopping it for 3 seconds.

Figure 3 illustrates the signals recorded for cadmium by applying the continuous and pulsed flow, respectively. Cadmium was considered very critical when applying the derivatization reaction because a spontaneous generation of cadmium free atoms is occurred from the hydride without any external effect (e.g. plasma).

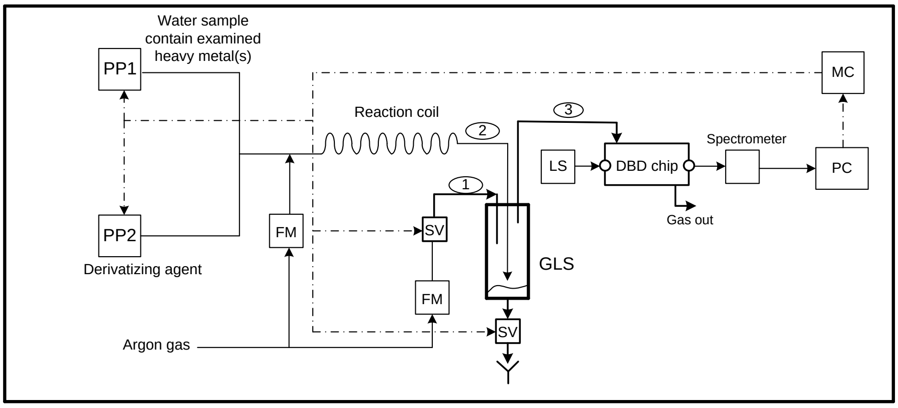


Figure 2. Automated system for determination of individual and multi heavy metals by applying oscillated gas-liquid separator. Note: PP: peristaltic pump, FM: flow meter, SV: solenoid valve, LS: light source, PC: Computer, MC: microcontroller interface, dotted line: signal transfer path, Experimental investigations for assessing the oscillated GLS performance.

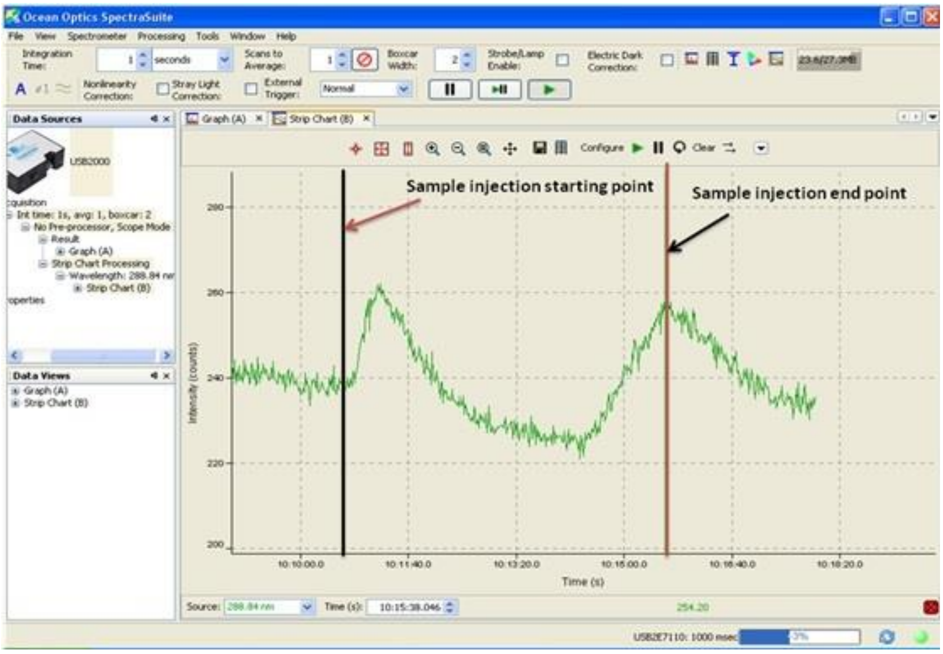


Figure 3. a) Cd derivatization, continuous gas flow 75 mL/min (without pulsing).

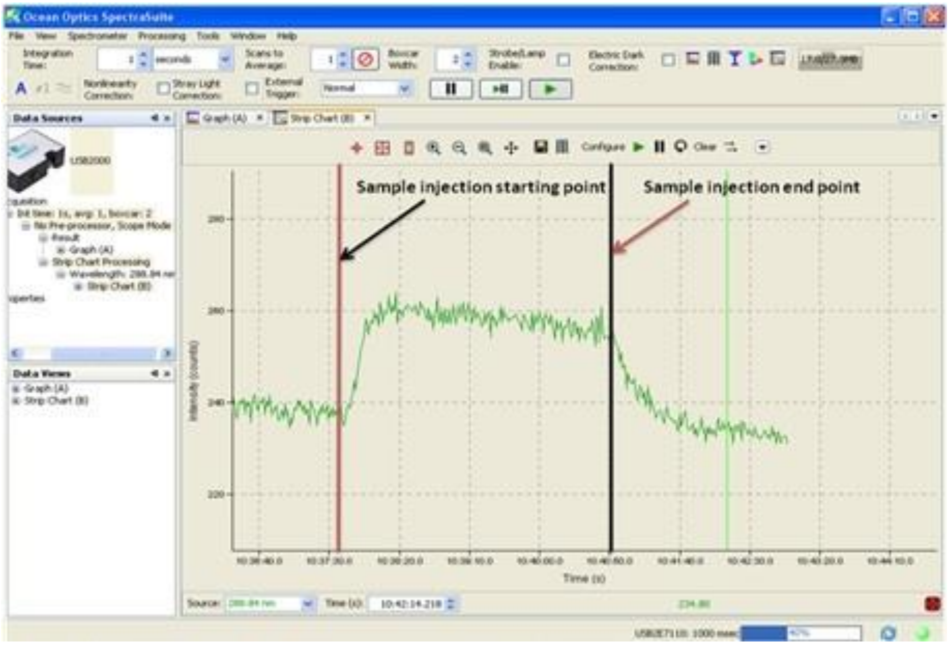


Figure 3. b) Cd derivatization, pulsed gas flow (75 mL/min for 4.0 seconds).

The signals recorded for cadmium has also been observed for the cases of tin and cupper, whereas the rest of the examined elements (Hg, As, Ni, Pb) have shown more stable performance in the cases of continuous and pulsed flow. Accordingly, three elements in the examined set were identified as critical (i.e. Cd, Sn, Cu).

On the other hand, approximately similar trend was observed when using lower gas flow rate (60 mL/min) in the continuous mode; nonetheless, the intensity became lower. In contrast, the disturbance became more obvious when applying higher flow rate in the continuous mode (90 mL/min). In any case, any kind of disturbance in the signal is not preferable and could lead to misleading when applying the quantitative determination.

The performance of GLS has also been investigated when applying the simultaneous detection of analytes. In the first experimental set, the critical elements were detected simultaneously by applying both modes of continuous and pulsed flow. **Figure 4** represents the signals recorded for the examined analytes in both cases by applying same reaction conditions (i.e. acidified water sample with 1.5 M HCl contains about 10 ug/L of each examined analyte and using 1.5% m/v $NaBH_4$ as a reducing agent). Green, pink, and black colored lines represents cadmium, cupper and tin respectively.

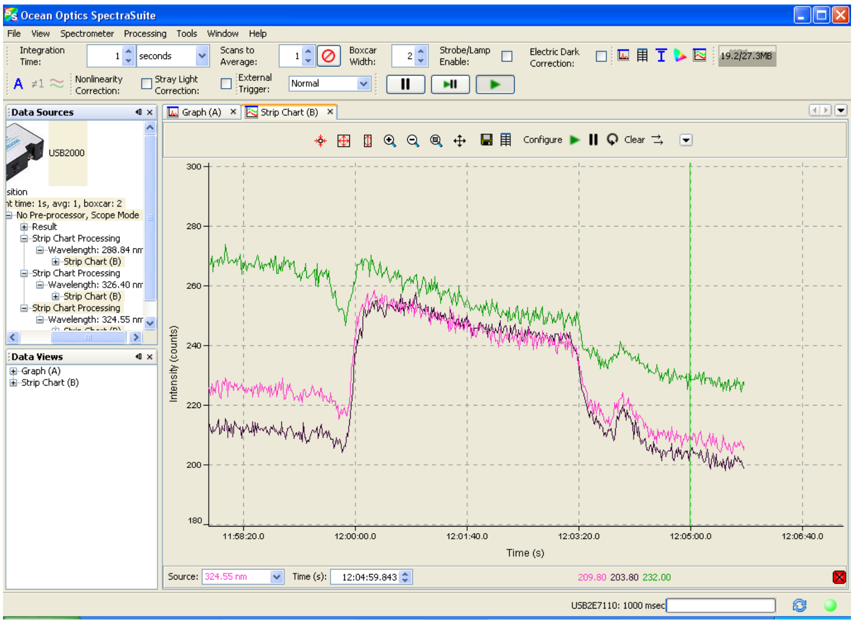


Figure 4. a) derivatization of Cd, Cu, Sn using 1.5% m/v $NaBH_4$ and applying continuous gas flow 75 mL/min (without pulsing).

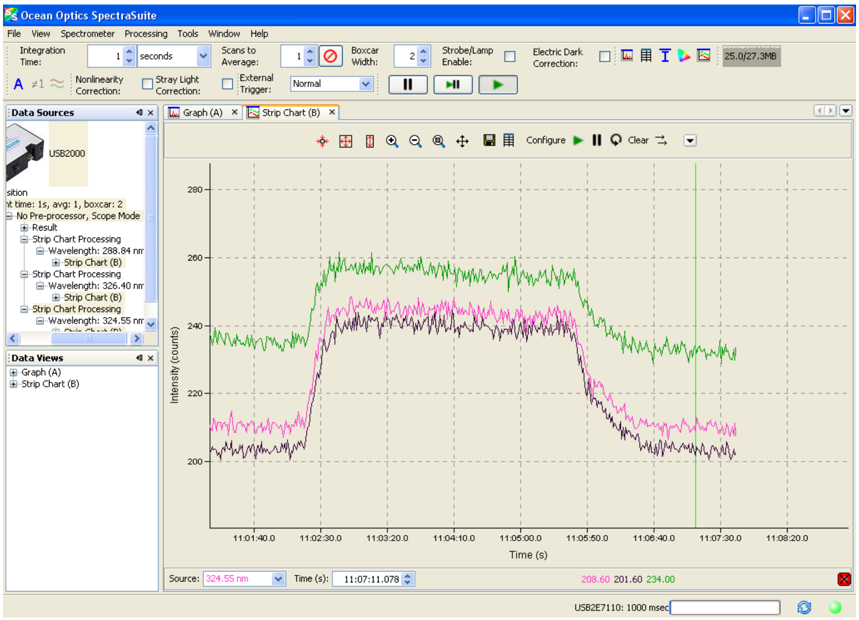
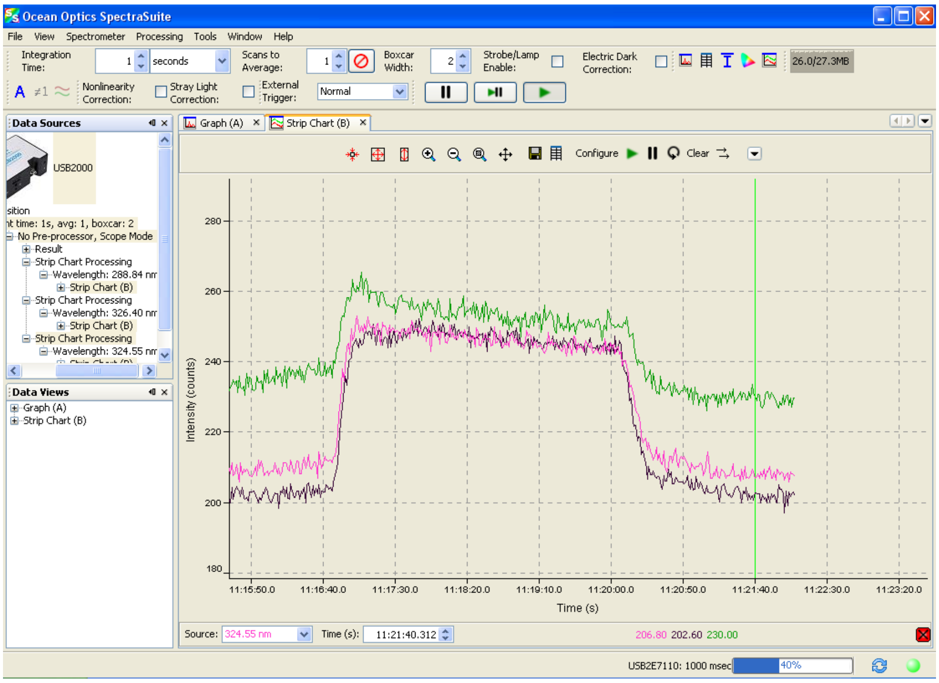


Figure 4. b) derivatization of Cd, Cu, Sn using 1.5% m/v $NaBH_4$ and applying pulsed gas flow (75 mL/min for 4.0 seconds).

Furthermore, the pulsed flow experiment was repeated by applying higher concentration of $NaBH_4$ (2% $NaBH_4$) as shown in **Figure 5**; this was to explore whether applying the pulsed flow is still beneficial or not when using higher concentrations of $NaBH_4$. It should be mentioned that the recorded signals for the case of using (2% $NaBH_4$) in the continuous flow mode have shown more discrepancy.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Scans to Average: 1
Boxcar Width: 2
Strobe/Lamp Enable: ☐
Electric Dark Correction: ☐
Nonlinearity Correction:
Stray Light Correction: ☐
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sition
nt time: 1s, avg: 1, boxcar: 2
No Pre-processor, Scope Mode
Result
Strip Chart Processing
Wavelength: 288.84 nm
Strip Chart (B)
Strip Chart Processing
Wavelength: 326.40 nm
Strip Chart (B)
Strip Chart Processing
Wavelength: 324.55 nm
Source: 324.55 nm
Time (s): 11:21:40.312
206.80 202.60 230.00
USB2E7110: 1000 msec 40%

Figure 5. Derivatization of Cd, Cu, Sn using 2.0% m/v $NaBH_4$ and applying pulsed gas flow (75 mL/min for 4.0 seconds).

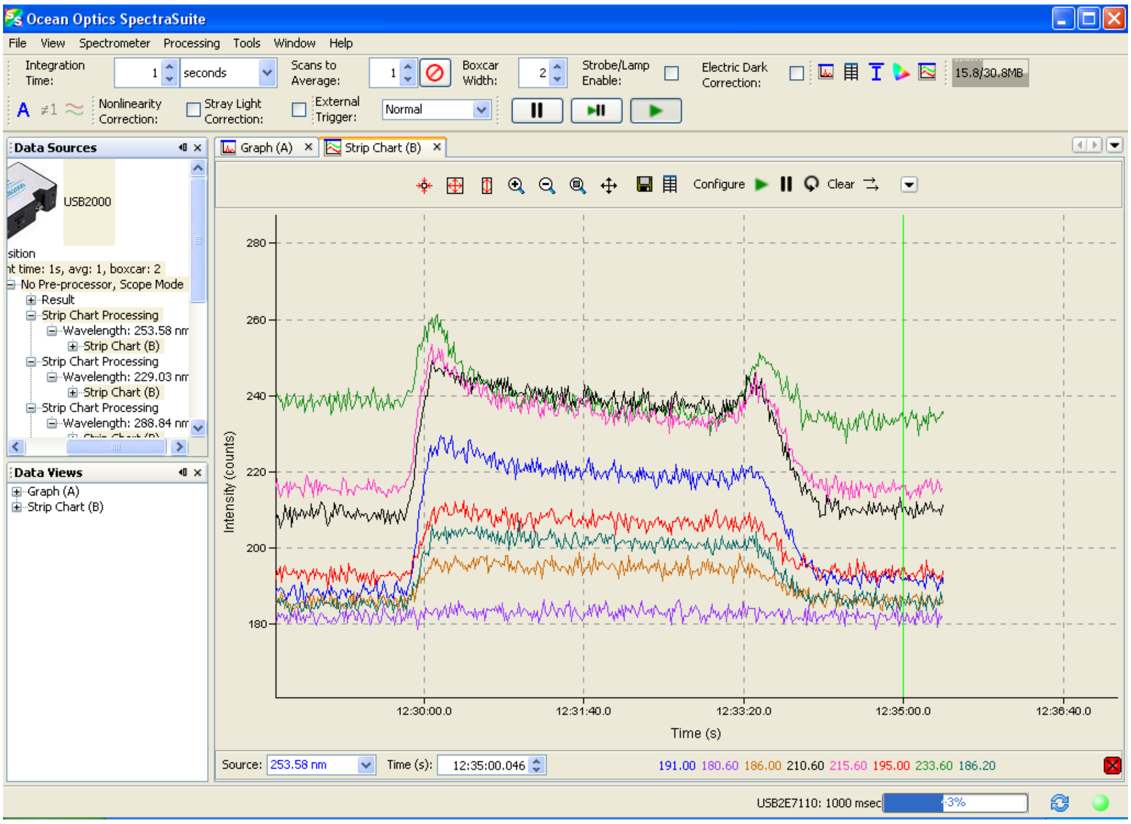
Integration Time: 1 seconds
Scans to Average: 1
Boxcar Width: 2
Strobe/Lamp Enable: ☐
Electric Dark Correction: ☐
Nonlinearity Correction:
Stray Light Correction: ☐
External Trigger: Normal
sition
nt time: 1s, avg: 1, boxcar: 2
No Pre-processor, Scope Mode
Result
Strip Chart Processing
Wavelength: 253.58 nm
Strip Chart (B)
Strip Chart Processing
Wavelength: 229.03 nm
Strip Chart (B)
Strip Chart Processing
Wavelength: 288.84 nm
Source: 253.58 nm
Time (s): 12:35:00.046
191.00 180.60 186.00 210.60 215.60 195.00 233.60 186.20
USB2E7110: 1000 msec 3%

Figure 6. a) 7 elements detection - continuous gas flow 75 mL/min (without pulsing).

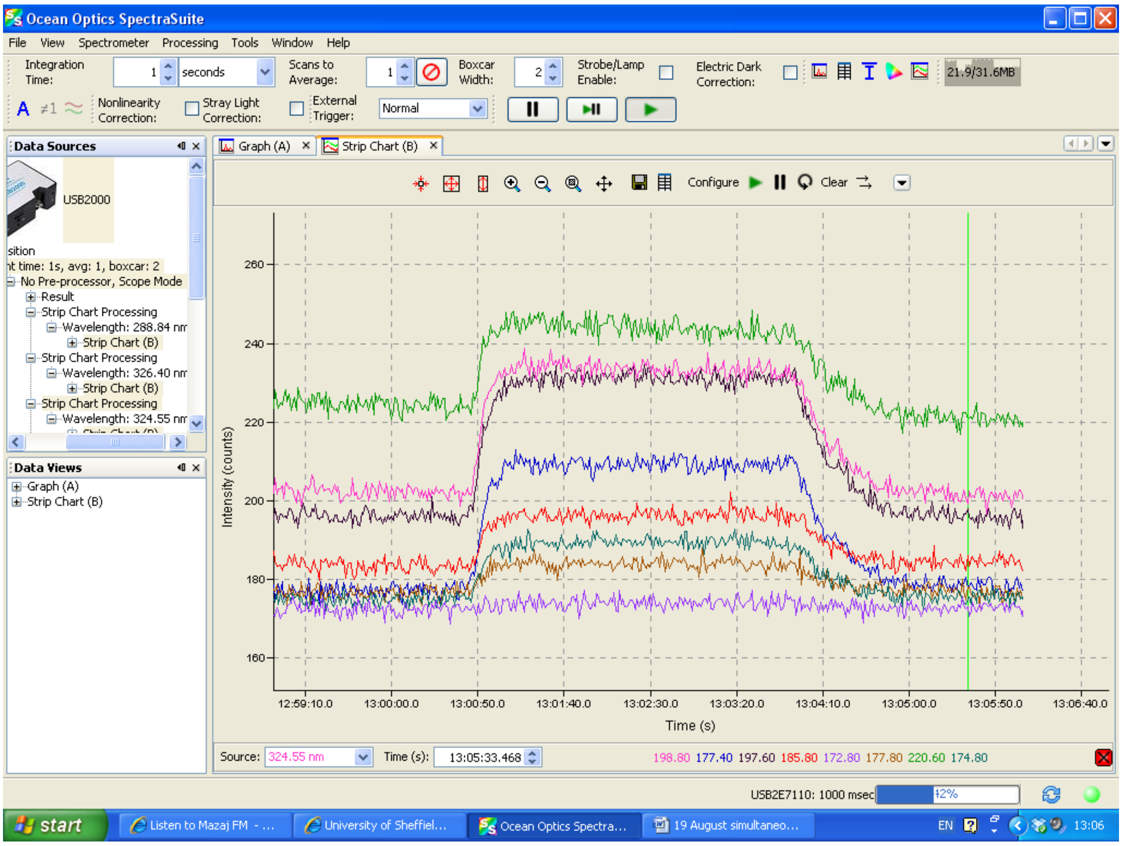
Integration Time: 1 seconds
Scans to Average: 1
Boxcar Width: 2
Strobe/Lamp Enable: ☐
Electric Dark Correction: ☐
Nonlinearity Correction:
Stray Light Correction: ☐
External Trigger: ☐ Normal
Source: 324.55 nm
Time (s): 13:05:33.468
198.80 177.40 197.60 185.80 172.80 177.80 220.60 174.80
USB2E7110: 1000 msec 12%

Figure 6. b) 7 elements detection - pulsed gas flow (75 mL/min for 4.0 seconds).

The simultaneous detection of seven heavy metals was implemented by applying the hydride generation reaction for an acidified water sample with 1.5 M HCl contains about 10 ug/L of each examined analyte and using 1.5% m/v $NaBH_4$ as a reducing agent. The gas liquid separator was operated by applying both continuous flow mode (75 mL/min) and pulsed flow mode (sequence form, 4 seconds with injection followed by 3 seconds without injection).

Figure 6 illustrates the recorded signals in both cases where the blue, red, olive and brown colored lines represent mercury, arsenic, nickel, and lead respectively. A violet line at (195.96 nm) was added to represent the stability of background signal.

3. Discussion

The main role of the GLS is to separate the gaseous phase from the liquid matrix upon completion of the reduction reaction. Therefore, design of the GLS should provide optimal separation of the aerosol droplets created by the bubbling action of the evolving gases, which results in signal disruption in the cases of poor separation. In order to understand the function of the gas pulsing on GLS performance, we should consider the massive disturbance which occurred to the whole spectrum upon being affected by extra quantity of hydrogen, as shown in **Figure 1**. It's worth noting that a tendency for aerosol and foam formation is highly possible in any kind of gas liquid separator especially when a huge amount of hydrogen is released to the GLS bulk. Thus, some researchers have considered the foam formation as highly effective on GLS performance; and hence, they used anti-foam agents with the injected samples to reduce this tendency[5]. Nevertheless, those anti foam chemicals could lead to signals interferences especially in the case of conducting simultaneous detection of multi heavy metals.

A probable reason for the improved signal result that obtained from applying the pulsed argon flow could be attributed to a lower hydrogen release rate from the liquid residues which are settled at the base of GLS. It was reported in the literature that extra hydrogen could be released from the liquid residues in the gas-liquid separator due to the instability of these residues. If a forced continuous stream of argon gas is injected toward the liquid surface, which is the case in the current GLS, then hydrogen stripping from the liquid residues would become easier.

Accordingly, the pulses of argon gas result in a gentle argon flow as well as a stable gas bulk inside the GLS, and consequently facilitate the transportation of the generated hydrides from GLS bulk to the DBD atomizer without further hydrogen generation from the liquid residues.

In general, and according to the recorded signals, three elements (Cd, Cu, and Sn) were found more vulnerable to the effect of hydrogen compared to other elements and defined as "critical". The reason could be interpreted from the spectrum shown in **Figure 1** where the top section shows the full spectrum before being subjected to the disturbance from the generated hydrogen. It can be observed in **Figures 4 and 5** that the emission lines of the critical elements [Cd (288.84 nm), Cu (324.55 nm), and Sn (326.375 nm)] are located at positions in the spectrum which were extremely disturbed upon being subjected to the hydrogen effect. The mostly affected area in the spectrum (around 300 nm) has been identified with existence of molecular N_2 in the region (337–380 nm) whereas the bands between (280–285 nm) and (302–317 nm) were defined as OH molecular emission lines. In addition to the abovementioned, the lines at (391.4 and 427 nm) were attributed to the N_2^+ molecular bands[6]. It seems that the identified species in the defined regions above were affected massively due to the hydrogen effect; therefore the signals recorded for the critical elements have shown instability (a gradual increase when the reaction started—a gradual decrease when the hydrogen entered to the atomizer—and finally a gradual increase when the sample injection stopped and the hydrogen become less in the system). Other elements were found more stable due to the positions of their emission lines in the spectrum, which is far from the mostly affected region. Even when the concentration of $NaBH_4$ increased to 2% m/v, the recorded signals of critical elements were found stable in the pulsed mode which indicates the performance of GLS is still reasonable.

4. Conclusions

In conclusions, applying the pulsed argon flow in the gas liquid separator has resulted more stable performance and relatively higher signal intensities even when applying higher concentration of $NaBH_4$. This improvement could be more obvious when applying the quantitative determination of multi heavy metals.

Conflict of interest

No conflict of interest was reported by the author.

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