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SPECTROSCOPY

Sensitive Detection of Metal Concentrations in Aqueous Solution Using Real-Time Micro-Plasma Emission Spectroscopy

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ABSTRACT
The global demand for green energy stimulates the need for rechargeable batteries and their components, containing lithium, cobalt, manganese, copper, and nickel. Consequently, the quantitative determination of the battery metals has crucial importance in optimizing associated processes and waste management. The fundamental properties of an analyzer for continuous process and field measurements are sensitivity, selectivity, stability, mobility, and robustness. Unfortunately, these characteristics are lacking in numerous existing methods for metals monitoring. Hence, this gap led us to demonstrate the performance of micro-discharge optical emission spectroscopy (μDOES), a novel online trace metal analyzer. This study shows that the new online analyzer with its simple and compact design can match requirements for real-time determination of metals in aqueous solutions in the field. The performance of the system is defined with copper, nickel, and lithium dissolved in deionized water. The limit of detection (LOD) along with long-term repeatability for Cu, Ni, and Li in continuous analysis reached 0.9, 4.1, and 0.1 μg/L, and 2, 2, and 4.2%, respectively. The applicability of the technique to a real-world application is demonstrated by analyzing a hydrometallurgical black mass sample received from the recycling process of lithium-ion batteries.

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Micro-discharge; micro plasma emission spectroscopy; on-site monitoring; trace metal analysis

Introduction

Over the last two decades, rechargeable lithium-ion batteries (Maggetto and Mierlo 2001; Nitta et al. 2015) have dominated electric vehicle, military, and aerospace applications to achieve the global target of ensuring clean energy. The rocketing demand has escalated the production of lithium-ion batteries, which eventually challenged the current waste management systems (Li et al. 2019; Boyden et al. 2016). Those discarded lithium-ion batteries may contaminate soil, groundwater, and surface water *via* leaching and disintegration (Mrozik et al. 2021) leading to a negative impact on the

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environment. However, research and development on the second-life use of electric vehicle batteries, along with efficient and safe processes for black mass recycling, is a promising way to tackle the problem. The European Directive 2006/66/EC, the current instruction on batteries in Europe, is being updated with more stringent requirements for re-use and recycling (Press Service, European Parliament, “Making batteries more sustainable, more durable, and better-performing” June 14, 2023). Therefore, a robust, sensitive, and real-time analytical procedure is required to monitor metal concentrations in the environment, industrial, and hydrometallurgical processes.

For metal detection in laboratories, conventional off-line analytical techniques such as atomic absorption spectroscopy (AAS) (Ferreira et al. 2018; Robinson 1960), inductively coupled plasma optical emission spectrometry (ICP-OES) (Kiran and Raja 2017) and inductively coupled plasma-mass spectrometry (ICP-MS) (Olesik et al. 1996; Wilschefski and Baxter 2019) are widely used. AAS can provide a high degree of accuracy, with a limit of detection in the µg/L range (Shaltout and Ibrahim 2007). The sensitivity of ICP-OES is also in the range of sub µg/L for As, Al, Cd, Cr, Cu and Pb in spiked wastewater samples with the introduction of microwave-assisted digestion (Dimpe et al. 2014). With ICP-MS, typical limits of detection (LODs) for metals in water are in the sub-µg/L range for Li, As, and Sb, with the best LODs as low as 0.01 ng/L for Lu, Tm, Tb, Ho, and Pr (Stetzenbach et al. 1994). However, those methods remain unsuitable for on-site application due to high power, requirement of inert gas, sample preparation, the use of nebulizer, complex instrumentation, and high cost per analysis.

The introduction of miniaturized plasmas has significantly overcome a few challenges associated with those of conventional discharge. Miniaturized plasma, or micro-plasma (Becker et al. 2006) is a special class of electrical discharges confined to dimensions of 1 mm or less. A microplasma source (Jo et al. 2008) is operable at atmospheric pressure and consumes modest power, making it a compact and cost-effective candidate for on-site measurements. In the last few decades, some significant advances have been reported for micro-discharges such as electrolyte cathode discharge atomic emission spectroscopy (ELCAD), solution cathode glow discharge (SCGD), atmospheric pressure glow discharge (APGD), and liquid electrode plasma atomic/optical emission spectroscopy (LEP-AES/OES).

ELCAD, introduced in the 1990s, shows good performance in multimetal analysis in the sub-mg/L range of aqueous solutions (Cserfalvi and Mezei 1994). The idea of SCGD was introduced in 2005 to provide a simplified ELCAD design (Webb et al. 2005) and is considered to be one of the most convenient microplasma sources to determine metals such as Li, Ni, Cd, Cu, Na in the µg/L range. Atmospheric pressure glow discharge (Kanazawa et al. 1998) was introduced in 1988 with the advantage of eliminating vacuum systems. A more recent study (Jamróz et al. 2012) reported that a miniature APGD operating in open air could determine Ca, Cd, Cu, K, Zn and Li in the range 2–100 μg/L. In liquid electrode plasma discharge, microplasma is generated without high power or carrier gas (Liduka et al. 2004). Another group (Kitano et al. 2011) has developed highly sensitive LEP-AES by combining a quartz glass chip and a sample flow system with detection limits of 0.52 μg/L for Cd and 19.0 μg/L for Pb. Recently, some commercial metal analyzers (Barua et al. 2020), based on liquid electrode plasma, have become available with detection limits ranging from 2 µg/L to 100 mg/L, depending on the element. Although microplasma-based systems (Zhang et al. 2021) demonstrate high potential for water analysis, the reported applications for on-site and continuous 24/7 water monitoring are still very limited.

In parallel with the microplasma methods, there are several widely used online or *in situ* techniques such as stripping voltammetry (SV), total reflection X-rays fluorescence (TXRF), spectrophotometry or spectrophotometry coupled with flow injection analysis (FIA/UV–Vis) which can be compared with µDOES.

Stripping voltammetry (SV) is an important method that performs multi-elemental analysis with high sensitivity between µg/L and mg/L. However, the lower temporal resolution of this method (Holmes et al. 2019) could affect the analysis. TXRF (Ruiz 2022) is another highly sensitive, fast, and precise spectrofluorometric method with detection limits between a few µg/L and a few thousand mg/L. However, it cannot be applied to quantify light elements (atomic number $<$ 13) such as lithium. Spectrophotometry (Ali et al. 2022) is similarly an easy, fast, and economical technique for metal analysis, but its performance is limited due to matrix interference. Flow techniques are characterized by ease of automation and, coupled with spectrophotometry, can determine trace metals in a few mg/L for different samples rapidly and accurately. However, the limitation involves preparing the samples based on different matrices (Costa et al. 2017).

Considering all essential parameters for real-time on-site analysis, we report a straightforward, robust, fast, and mobile system, designated as micro-discharge emission spectroscopy (µDOES), for metal determination in water samples. The presented commercial analyzer, developed by Sensmet, can continuously detect up to 30 dissolved metals in process water and natural water bodies. The sensitivity, in the range of µg/L, high linearity, repeatability, automatic sampling, and applicability in determining metals in real time have motivated us to demonstrate and evaluate its performance.

Experimental

Instrumentation

The principle of the µDOES analyzer is shown in Figure 1. A micro-discharge, i.e., an electric spark is created directly inside the aqueous sample. In an instant, a microscopic volume of the sample water surrounding the spark gets flash-heated to an order of 10,000 K. The plasma temperature can be estimated using the Boltzmann distribution with experimentally measured oxygen line intensities (Hussain et al. 2016), for example. Molecular species in the micro-discharge are dissociated into atoms, followed by excitation of the atoms to their respective higher electronic states. Upon returning to their ground state, atoms release their excess energy by emitting light at their characteristic wavelengths. Measuring the atomic emission spectrum enables the determination of the metals contained in the sample. As the micro-discharge is directly created inside the water sample, there is no need for a carrier gas like argon, which is typically consumed in ICP-OES and ICP-MS. The transfer of water samples into the plasma chamber is straightforward, as peristaltic pumps are used to deliver the sample into the plasma chamber, thus excluding the use of any nebulizers. The plasma emission is collected through an optical fiber and analyzed using a spectrometer.

In a typical measurement, high-voltage pulses are created at 500 to 1000 Hz repetition rates for plasma generation (Blomberg et al. 2012) inside a quartz tube (5 mL of sample

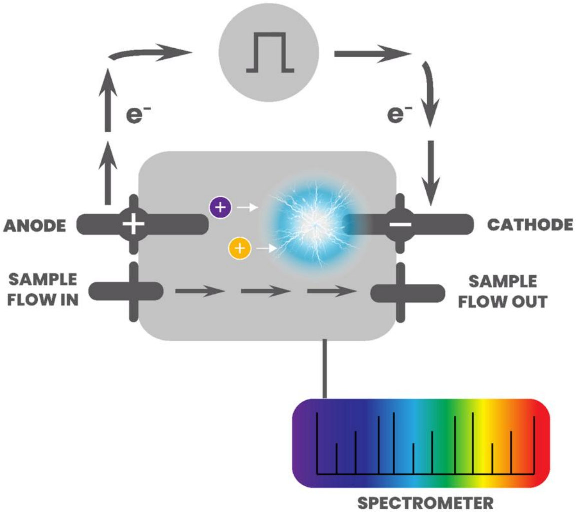

Figure 1. Principle of the micro-plasma instrument. A microscopic volume of the sample water surrounding the spark is flash heated to approximately 10,000 K emitting at characteristic wavelengths for each metal in the sample.

cell volume) between tungsten and graphite electrodes under standard atmospheric pressure. Although several combinations of electrode materials can be used, graphite was chosen for this study as it creates a spectrally clean background without many emission lines. The exposure time of the spectrometer is matched with the individual microplasmas to collect the emission spectrum. Depending on the application, the discharge voltage is up to a few kilovolts.

Sample preparation

Certified reference materials (CRM) of 10,000 mg/L supplied by Romil were used as the starting point to prepare the working standards. The stated uncertainties from the manufacturer's certificate for copper, nickel, and lithium concentrations are 26, 22, and 13 mg/L at the 95% confidence level. The high-purity deionized water from Merck (resistivity at 25 °C is 18.2 MΩ cm) was used to prepare the blank standards. The working standard solutions are prepared by serial dilution of the standard in deionized water.

In order to study the selectivity of the analyzer, a solution containing 0.1 mg/L of copper, lithium, and nickel was prepared in deionized water by pipetting the required volume from 10,000 mg/L. Additionally, to prepare copper and nickel calibrations, corresponding intermediate solutions around 1.75 mg/L concentration were prepared directly from the stock solution. Concentrations between 10–100 µg/L and 5–100 µg/L were generated in the analyzer's sample cell using the micropump. The preparation of the lithium working standard required an extra intermediate step. The first intermediate lithium stock solution of 1000 mg/L concentration was prepared from the 10,000 mg/L CRM standard solution, followed by dilution to the second intermediate solution of 0.175 mg/L. Lithium concentrations between 0.1 and 10 µg/L were generated using the micropump.

Finally, acknowledging the importance of black mass recycling nowadays, we demonstrate the analyzer's capability of metal determination in a liquid black mass sample.

Results and discussion

The performance of the µDOES multi-metal analyzer was evaluated through sensitivity, linearity and uncertainty in determining lithium, copper and nickel.

Emission spectra of metals

µDOES covers the spectral range from 200 nm to 840 nm. The identification of emission lines for each metal is typically based on comparing the emission lines with the established lines used with ICP-OES or the NIST atomic emission database (Ralchenko 2005), followed by analysis of the candidate emission lines to minimize spectral interference and matrix effects. Figure 2 shows the full emission spectrum of a multi-metal solution containing lithium, nickel, and copper at a sub-mg/L concentration. The spectrum consists of multiple atomic and ionic emission lines. For example, a series of nickel lines ranges from 341.23 to 362.12 nm. Based on the peak intensity, we focus our analysis on the following lines: Cu I at 324.702 and 327.314 nm, Ni I 341.38 and 351.50 nm, and Li I 670.791 nm. In the 275 nm to 315 nm range, the emission band of OH^- radical is visible. The strong emission lines at 486.1 and 656.2 nm correspond to ionic hydrogen. The ionic oxygen line appears at 777.19 nm. The intensity of the emission lines depends on the electrical conductivity of the samples. Hence, to achieve repeatable analytical signals, the electrical conductivity of each sample is automatically adjusted to a set level before each measurement. In this study, the conductivity was adjusted to 2500 µS/cm using 1% H_2SO_4.

Analytical performance

Generally, the limit of detection implies the smallest concentration of analyte that can be distinguished from a blank. Any data less than these values is statistically known as “censored data” (Helsel 1990). Detection limits are direct indicators of system

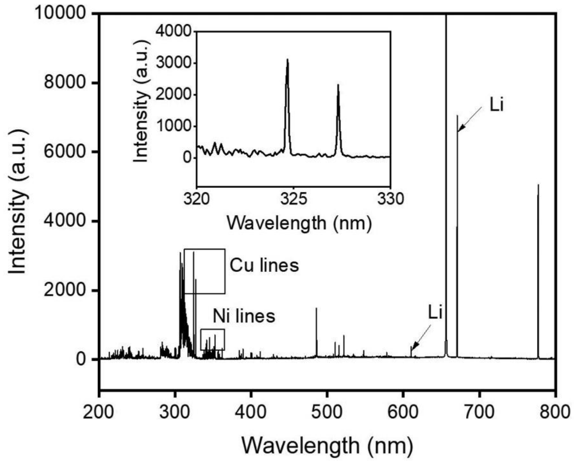

Figure 2. Emission lines of 0.1 mg/L copper, nickel, and lithium from a multi-metal solution. Inset: magnification of the copper 324.702 and 327.314 nm emission lines.

performance, making them an important parameter to compare with other techniques. In the literature (Shrivastava and Gupta 2011), there are different ways of determining the limit of detection. Regarding the signal-to-noise-ratio (SNR) based analysis, the signal is usually estimated from the maximum peak height of the analyte signal, and noise is determined from the root-mean-square variation of the blank.

For analytical purposes, we adopted here the conventional approach where the signal-to-noise ratio of three is considered to be the threshold for detecting the signal. The calibration model of pure metal spectrum is first fitted to the measured emission spectrum using the least squares method which improves precision and robustness of the analysis. The background level was determined by repeated fitting of the calibration model to blank measurements for each sample and followed by calculating the standard deviation of ten repeated blank measurements.

Use of a proper calibration model minimizes the effects due to the background, spectral interference and matrix interference. Figure 3 shows an example how background subtraction improves the appearance of low intensity copper signals.

For the analytical measurements, the µDOES analyzer was calibrated for copper and nickel from 10 to 100 µg/L and 5 to 100 µg/L, respectively, and for lithium from 0.1 to 10 µg/L. Every point is the average of three consecutive measurements.

To understand the quality of measurements, it is important to study the repeatability. Moreover, it is crucial to produce precise and reliable results during extended runs in laboratories or in the field. The repeatability test for copper, nickel and lithium was continued for 12 h and expressed as the relative standard deviation ($n = 100$). The analytical figures of merit are summarized in Table 1.

The limit of detection LOD was calculated by considering the wavelength range consisting of two closely spaced emission peaks for nickel and copper and one emission peak for lithium. A LOD of µg/L level or below for the metals indicates high sensitivity. The linearity (adjusted R^2) of 0.998 or better shows good potential for highly linear response. The relative standard deviation of <5% shows good repeatability of measurements over a long period of time. A comparative study on the sensitivity between µDOES and other micro plasma-based methods, such as ELCAD (Kim et al.2000),

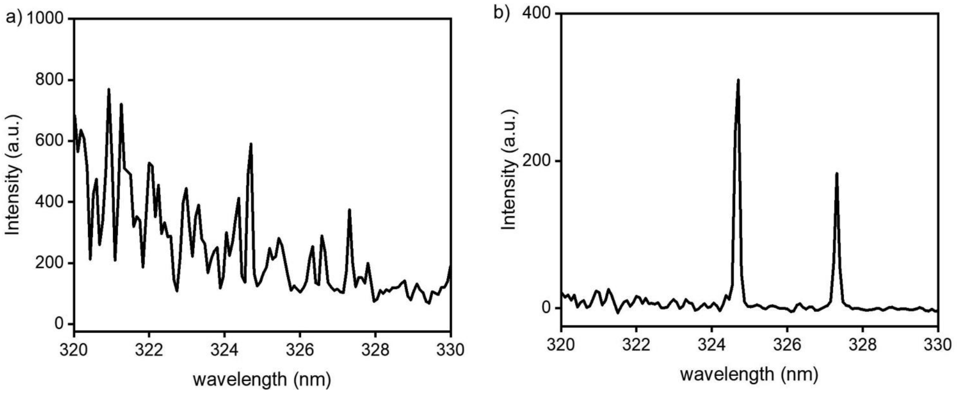

Figure 3. (a) Raw emission spectrum of 9.5 µg/L copper. The peaks at 324.702 and 327.314 nm are challenging to distinguish from background. (b) Copper peaks are more visible after subtracting the blank spectrum.

Table 1. Quantitative determination of copper, nickel, and lithium. The limit of detection (LOD) is determined to be three times the standard deviation of ten repeated measurements of the blank.

Element	Emission wavelength (nm)	Linear equation	Limit of detection (μg/L or ppb)	Linearity (adjusted R^2 values)	Relative standard deviation (%)
Copper	324.702 and 327.314	$1.001x - 0.041$	0.9	0.998	2
Nickel	341.38 & 351.50	$0.996x + 0.313$	4.1	0.998	2
Lithium	670.791	$0.998x + 0.017$	0.1	0.999	4.2

Table 2. Limit of detection (μg/L) comparison between μDOES and literature micro plasma methods.

Element	μDOES	ELCAD	APGD	SCGD	LEP-AES
Copper	0.9	10	80	31	11
Nickel	4.1	20	_	110	_
Lithium	0.1	_	2	8	_

APGD (Jamróz et al. 2012), SCGD (Webb et al. 2005) and LEP-AES (Nakayama et al. 2011) is shown in Table 2. Another comparison is also presented in Table 3 between μDOES and FIA-spectrophotometry (Memon et al. 2012; Zenki et al. 2002), stripping voltammetry (Amayreh et al. 2021; Padilla et al. 2021), total reflection x-ray fluorescence (Malkov et al. 2017), and spectrophotometry (Ali et al. 2022; Mossotti et al. 2023).

Uncertainty analysis

The uncertainty of the prepared metal concentrations of Cu, Ni, and Li for the LOD and linearity was defined according to the literature (Ellison and Williams 2012; Karakas 2007). The uncertainty budget of copper is shown in Table 4 as an example. Identification of the uncertainty sources was performed using a fishbone diagram as shown in Figure 4.

The first uncertainty component arises from the certified reference material concentration C and is specified by the manufacturer as 10,000 mg/L with 26 mg/L expanded uncertainty at 95% confidence level ($k = 2$). Hence, the standard uncertainty is given by $u(C) = 13$ mg/L.

The second component originates from the volume uncertainty of the 1-litre flask and repeatability associated with the preparation of the solution. According to the literature (Ellison and Williams 2012), a triangular probability distribution was used to calculate the standard uncertainty from the certified volume given as 1000 mL with 10 mL uncertainty leading to 4.1 mL. The standard uncertainty due to filling the flask was obtained from standard deviation of a series of repeated ($n = 20$) filling and weighing experiments resulting in 0.42 mL. Both contributions are combined to give the standard uncertainty $u(V_f)$ of volume V_f as $u(V_f) = \sqrt{4.1^2 + 0.42^2}$ mL = 4.1 mL.

The third uncertainty component is related to the intermediate solution prepared with a pipetting volume V_p of 0.175 mL. The volume was determined from repeated filling and weighing measurements ($n = 20$) resulting in the standard uncertainty $u\ (V_p)$ of 0.0027 mL. The individual concentrations were prepared using the analyzer micropumps for automated dilution from the working standards. The uncertainty due to automatic sampling was determined by repeating the weighing experiments. The micropump dispensing volume V_m was 0.0279 mL and the sample cell volume V_s was 47.5 ml. Hence, the standard uncertainties from micropump $u\ (V_m)$ and sample cell $u\ (V_s)$ were

Table 3. Limit of detection (μg/L) comparison of μDOES with other literature methods.

Element	μDOES	FIA-spectrophotometry	SV	TXRF	Spectrophotometry
Copper	0.9	60	180	0.16	7
Nickel	4.1	10	0.5	0.15	300
Lithium	0.1	_	_	_	_

Table 4. Uncertainty budget for the copper concentration.

Parameter (unit)	Value (X)	Standard uncertainty $u(X)$	Relative standard uncertainty $u(x)/X$ (%)
Stock solution concentration C (mg/L)	10 000	13	0.13
Volume of the flask V_f (mL)	1000	4.1	0.41
Pipette Vp (mL)	0.175	0.0027	1.5
Micropump V_m (mL)	0.0279	0.0011	3.9
Sample cup V_s (mL)	47.5	0.056	0.12
Combined standard uncertainty (u)			4.2

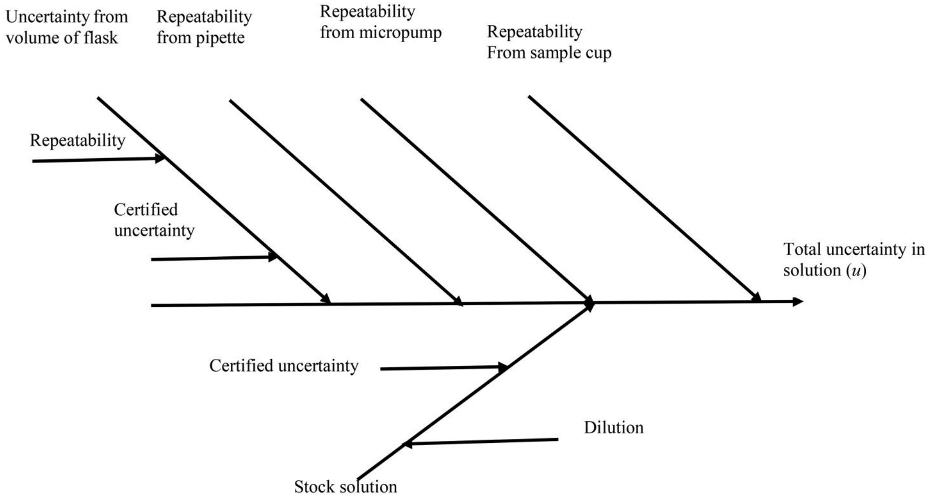

Figure 4. Fishbone diagram to analyze the uncertainty.

calculated from standard deviations of series of repeated ($n = 10$) measurements, resulting in 0.0011 and 0.056 mL, respectively. Finally in Table 4, each uncertainty is expressed as relative uncertainties and combined relative standard uncertainty is calculated from quadratic equation: $u = \sqrt{\frac{u(C)^2}{C} + \frac{u(V_f)^2}{V_f} + \frac{u(V_p)^2}{V_p} + \frac{u(V_m)^2}{V_m} + \frac{u(V_s)^2}{V_s}}$.

Table 4 shows that the relative standard uncertainty of copper solutions is 4.2%. The uncertainty for nickel was calculated in the same way leading to a relative standard uncertainty of 4.2%. As the preparation of lithium solution consisted of two intermediate steps, the uncertainty analysis of lithium samples needs to cover the dilution from 10,000 to 1000 mg/L, followed by the dilution from 1000 to 0.175 mg/L, which results in 4.3% relative standard uncertainty.

Example leached black mass analysis

To demonstrate the applicability of the technique, we present an example spectrum of a leached aqueous black mass sample. Black mass (Sommerville et al. 2021) is a mixture of metals such lithium, nickel, copper, manganese, and cobalt obtained from recycled lithium-ion batteries.

After leaching into the liquid phase, the hydrometallurgical black mass samples require no other pretreatments than dilution before analysis. Figure 5(a) shows the emission spectrum of an aqueous, diluted black mass sample introduced to the analyzer. The emission lines for nickel and copper are provided in Figure 5(b) and (c). The peaks are visible after eliminating the background from the spectra, indicating the analyzer's efficiency without time-consuming sample treatments. The black mass sample was also analyzed in an independent laboratory by ICP-OES. Table 5 shows good agreement with the reference method.

Conclusion

The analytical performance of a new online micro-plasma analyzer for quantifying the concentration of multiple metals in aqueous samples has been presented. The novelty of the analyzer lies in automated and robust on-line monitoring of trace metals over long periods of time. Hence, it is important to assess the capabilities of the instrument, based upon the sensitivity, linearity, and long-term repeatability. The determination of copper, nickel and lithium at low µg/L concentrations indicates that the instrument can be applied to environmental and industrial applications.

For example, Li concentrations from 0.01 to 17.5 mg/L have been reported in surface waters (Adeel et al. 2023) which matches the linear range of the analyzer. Together with its mobility and robustness, µDOES can also target on-site applications where metal concentration data are required in real time. In this study we demonstrated the applicability of analyzer for high-impact hydrometallurgical black mass samples from recycled lithium batteries. Novel measurement approaches, automated from sampling to the presentation of the analytical results, are required for industrial process control and environmental monitoring. Online monitoring benefits include reduction in manual labor and avoiding errors associated with manual sampling, sample transportation, and

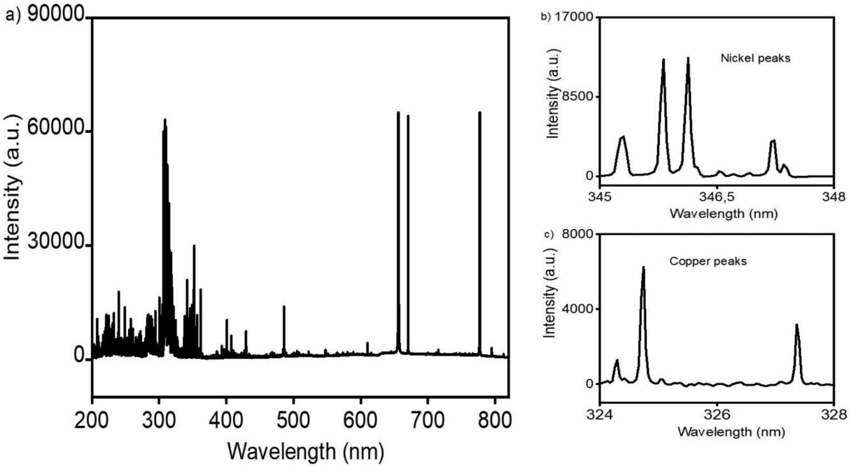

Figure 5. (a) Raw emission spectra from black mass. (b and c) Major peaks for nickel and copper after eliminating the background.

Table 5. Comparison of black mass analysis by µDOES and ICP-OES reference technique.

Metal	µDOES (mg/L)	ICP-OES (mg/L)
Copper	845	846
Nickel	55,959	55,685
Lithium	10,515	10,509

pretreatment. With its simplified approach, the investigated metal analyzer can find wide applications in process water applications such as metals production and recycling, water quality analysis at powerplants, and semiconductor industry. Furthermore, as the technology is still new, it has great opportunities for future research and development.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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