

Selenium quantification in wastewaters from selected coal-fired power plants and river waters in South Africa using ICP-MS

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South Africa mainly relies on Eskom's coal-fired power plants for electricity generation. However, the use of coal causes several adverse environmental impacts, including the release of selenium into the hydrosphere. Selenium is an essential nutrient for humans, animals, and microbes, but excess selenium is toxic. This paper describes the determination of total dissolved selenium in wastewater from selected coal-fired power plants and river waters near coal-fired power plants in South Africa. A sensitive and robust inductively coupled plasma mass spectrometry (ICP-MS) method for determining total dissolved selenium in wastewater and river water was developed using a certified reference material (NIST SRM 1640a Trace Elements in Natural Water). The results agreed with the certified values, with percentage recoveries ranging from 92–96%. The method detection limit was 0.13 µg/L. Total Se concentrations in wastewater samples from Kriel and Lethabo Power Stations ranged between 4.86 and 8.53 µg/L, and in river water samples from the Olifants and Wilge Rivers, the concentrations ranged from 2.63–8.20 µg/L. These results indicate that the Se levels in the wastewater are too low to pose a health hazard to humans and livestock but pose an environmental threat to aquatic life. The low concentrations in the river samples also show that there may be slight Se pollution (regarding aquatic life) from the selected coal-fired power plants in South Africa. There may be slight Se pollution (with regards to aquatic life) from Duvha and Kendal Power Stations because an increase from 2–8 µg/L was observed in river water samples collected near these selected coal-fired power plants.

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INTRODUCTION

The use of coal in South Africa, primarily for electricity generation, is unlikely to change significantly in the next few decades owing to the relative lack of suitable alternatives (Doyle, 2015). The use of this fossil fuel, nonetheless, is one of the prime anthropogenic activities that pollute the atmosphere, biosphere, and hydrosphere (Zvereva and Krupskaya, 2013; Hendryx et al., 2020). Pollutants emanating from coal and coal combustion include particulate matter, sulphur dioxide (SO₂), nitrogen oxides (NO_x), heavy metals, and trace elements (Hg, As, Se, Cd, Cr) (Simons, 1993; Dabrowski et al., 2008; Xu et al., 2017). Some pollutants partition into the water used extensively in various stages of power generation. The power plants generate highly contaminated wastewater (Ribeiro et al., 2010; Vig et al., 2022).

The scientific literature on South African water and wastewater reveals a strong focus on physicochemical parameters (pH, electrical conductivity, temperature, dissolved oxygen, total dissolved solids, alkalinity, hardness), nutrient load (Cl, SO₄, NO₃, NH₄), and total concentrations of major and minor elements (Al, Cr, Fe, K, Mn, Na, Zn) (Edokpayi et al., 2017; Agoro et al., 2018; Nyamukamba et al., 2019; Madilonga et al., 2021). The literature shows a lack of information on the concentration of toxic trace elements (As, Cd, Hg, Se and Pb) in wastewater from South Africa's coal-fired power plants. An element of particular interest is selenium (Se), also derived from coal. Selenium is essential in trace amounts for humans, animals, and many organisms due to its antioxidant effects and as a constituent of selenoproteins (Weekley and Harris, 2013; Hossain et al., 2021). However, exposure to large amounts of Se and its salts can be toxic and may cause neurotoxic effects (Vinceti et al., 2014; Ding et al., 2022), unsteady gait, fever, nausea, hair loss, liver, kidney, and heart problems (Kumkrong et al., 2018). Selenium is a chalcogen associated with sulphur-containing minerals, particularly high-sulphur coals (Gorchev and Ozolins, 2011; Lenz and Lens, 2009); consequently, process and wastewater streams from coal-fired power plants can contain elevated concentrations of selenium, far exceeding many discharge limits (Petrov et al., 2012; Stefaniak et al., 2018).

The total content of Se provides a valuable indication of deficiency or pollution intensity. Analysis of Se has been complex, mainly because environmental concentrations are naturally low. Recent improvements in analytical methods enable the routine determination of Se in water samples, even at low concentrations (Johnson et al., 2009; Etteieb et al., 2020a). Regulations are becoming increasingly stringent because Se tends to bioaccumulate up to 100–350 000 times. The implication is that even a trace concentration of 0.1 µg/L in wastewater can easily be elevated to toxic levels; hence, there is a need for analytical methods capable of accurately analysing sub-µg/L concentrations of Se in the presence of interfering matrix components (Lemly, 2004; Tan et al., 2016). Various discharge limits have been set depending on country and region; for instance, the effluent water discharge limit in British Columbia, Canada, is 2 µg/L, while in Japan and Korea, it is 100 µg/L and 1 µg/L, respectively (Tan et al., 2016). United States Environmental Protective Agency (USEPA) wastewater hazard index is 5 µg/L for chronic aquatic life toxicity (Santos et al., 2015) and 20 µg/L for acute aquatic life

toxicity (Park et al., 2016; Tan et al., 2016). South Africa's upper limit gazetted by the Department of Water Affairs and Forestry (DWAF) for total selenium in drinking water and water for livestock is 50 µg/L; the limit for water for human consumption and irrigation is 20 µg/L, and the limit for freshwater for aquatic life is 2 µg/L (DWAF, 1996a; DWAF, 1996b).

To comply with these regulations, analytical methods that have been used to quantify total Se include colourimetry, total reflectance-x-ray fluorescence (TXRF) (Li et al., 2014), hydride generation atomic fluorescence spectrometry (HG-AFS) (Shishov et al., 2018), flame atomic absorption spectroscopy (FAAS) (Pettine et al., 2015), graphite furnace-AAS (GF-AAS) (Zacharia et al., 2018), voltammetry (Ashournia and Aliakbar, 2009; Devi et al., 2017), ICP-MS (Etteieb et al., 2020b), and inductively coupled plasma optical emission spectrometry (HG-ICP-OES) (Tyburska et al., 2011; Luo et al., 2017). The American Society for Testing Materials (ASTM) D 3859-08 standard test methods for selenium in waters and wastewaters include the determination of dissolved and total recoverable Se. Two less expensive and widely applied methods are atomic absorption techniques, for example, gaseous hydride AAS and GFAAS (ATSDR, 2003). In the past, fluorimetry was commonly used to determine Se in environmental samples, but more sensitive instrumental methods are replacing it. ICP-OES and ICP-MS are presently the most utilised techniques (Gu et al., 2015; Wiczorek et al., 2017; Etteieb et al., 2020b; Okonji et al., 2021) for Se quantification in aqueous samples. ICP-MS detection of Se is more favoured because of its sensitivity, even without hydride generation or other forms of preconcentration. It offers good selectivity, much simpler spectra than optical techniques, low detection limits (ng/L–µg/L depending on the cleanliness of the laboratory), wide dynamic range, the ability to take isotopic measurements, and low sample consumption (Nemeth and Dernovics, 2015; Kumkrong et al., 2018). Aqueous samples that are analysed using ICP-MS usually require the least sample preparation.

Selenium has been an important subject in numerous investigations because of its dual role as an essential trace element for humans, animals, organisms, and crops, but detrimental at high concentrations. A literature survey reveals that although Se pollution and deficiency is a global concern, there have been no efforts to address this issue in Southern Africa. This lack of effort in addressing this concern is alarming, especially considering that coal mining and combustion (some of the major anthropogenic sources of Se) have been and continue to be practised at a large scale in this region. To address this issue, our study investigated total Se in the effluent (treated wastewater samples) from selected coal-fired power plants and selected rivers (also close to coal-fired power plants).

In view of the above, this study reports a method developed for the determination of Se in wastewater from coal-fired power plants and river water. The developed method was successfully applied to treated wastewater samples from Kriel and Lethabo Power Stations and Wilge and Olifants Rivers water samples. It was important to develop a robust ICP-MS method for the determination of total dissolved Se in both effluent and river water with the least sample preparation and offering very low LOD (which was achieved because samples were only filtered, acidified and analysed). LOD values can be compared with those reported in previous studies (Kumkrong et al., 2018). This is crucial so that the method can be used routinely to analyse effluent and river water samples. It should be noted that the method incorporated ⁸⁹Y as an IRS rather than the routinely used ⁷²Ge. The ⁷²Ge was (i) highly interfered with by ⁵⁶Fe¹⁶O⁺ because of the Fe present in the samples (generally, Fe is present in many water samples, and it is crucial to use an IRS with the least or no interferences), and (ii) trace amounts of ⁷²Ge were observed in the samples, and this would inevitably skew the overall results.

This was pivotal in indicating Se status in wastewater from coal-fired power stations and natural waters near the power plants and assessing regulatory compliance. The study facilitates both managerial and technological solutions to the quantification of Se and is vital in making more accurate assessments of the environmental impact and health risks. This study also opens the doorway for more research to be carried out and to gather significant data for South African regulatory bodies to make informed decisions regarding Se. Countries such as the USA, Canada, UK, France, Germany, India, Japan and China have set discharge limits for Se, and a developing country such as South Africa should also develop its limits through investigations similar to our study rather than solely rely on or adopt umbrella discharge limits set by international organisations.

METHODS

Sampling

The first batch of samples was received from the Lethabo Power Station (located between Vereeniging and Sasolburg in the Free State Province) and the Kriel Power Station (located between the towns of Kriel and Ogies in the Mpumalanga Province). The sampling points at Lethabo indicated in Fig. 1 were ash dam toe-drains, coal stockpile run-off, cooling towers, and dirty drains. The same sampling points were selected at Kriel, excluding the cooling towers sample. Figure 2 illustrates these selected sampling sites. The second set of samples was collected at Olifants River Site A and Site B (see coordinates in Table 1) near Duvha Power Station, approximately 15 km east of eMalahleni in Mpumalanga, and Wilge River near Kendal Power Station located 40 km southwest of eMalahleni in the Mpumalanga district.

The GPS coordinates for all the sampling sites are shown in Table 1. Sampling at Lethabo and Kriel Power Stations was done during the dry season (i.e., from late April to June), while sampling at Olifants and Wilge Rivers was done during the onset of the wet season in November. Lethabo Power Station is located within Fezile Dabi District Municipality, and during the dry season the area receives an average rainfall of 2.5 mm. Temperatures can vary from –1°C to 20°C and relative humidity from 20% to 90% in winter (Weather Spark, 2023; DMR, 2017). Kriel Power Station and the selected sampling sites at Olifants and Wilge Rivers fall under Nkangala District Municipality. During the wet season, the rainfall received varies from 180–500 mm, and the average minimum and maximum temperatures are 10°C and 35°C, respectively (NDM, 2015).

During each sampling programme, the physicochemical parameters measured were temperature, pH, and electrical conductivity (EC). Water samples were collected using a clear acrylic Kemmerer Sampler for surface water and a beaker scoop similar to the Telescope beaker scoop (600 mL) for the shallow regions of the rivers. Samples were filtered through 0.45 µm filter paper into high-density polyethylene (HDPE) bottles. Each filtered sample was preserved in 1% HNO₃, transported in a portable ice chest with ice to the laboratory, and stored in the refrigerator at 4°C before analysis.

Table 1. GPS coordinates for sampling sites

| Sampling area | GPS coordinates |
|-----------------------|------------------------------------|
| Lethabo Power Station | 26° 44' 29.89" S; 27° 58' 22.19" E |
| Kriel Power Station | 26° 14' 59.53" S; 29° 10' 34.81" E |
| Olifants River Site A | 25° 58' 22.80" S; 29° 17' 07.30" E |
| Olifants River Site B | 25° 55' 17.59" S; 29° 18' 23.75" E |
| Wilge River | 26° 01' 59.20" S; 28° 51' 43.80" E |

Olifants River Site A and Site B are referred to as Olifants River Influent and Olifants River Effluent, respectively, in Tables 3 and 4.

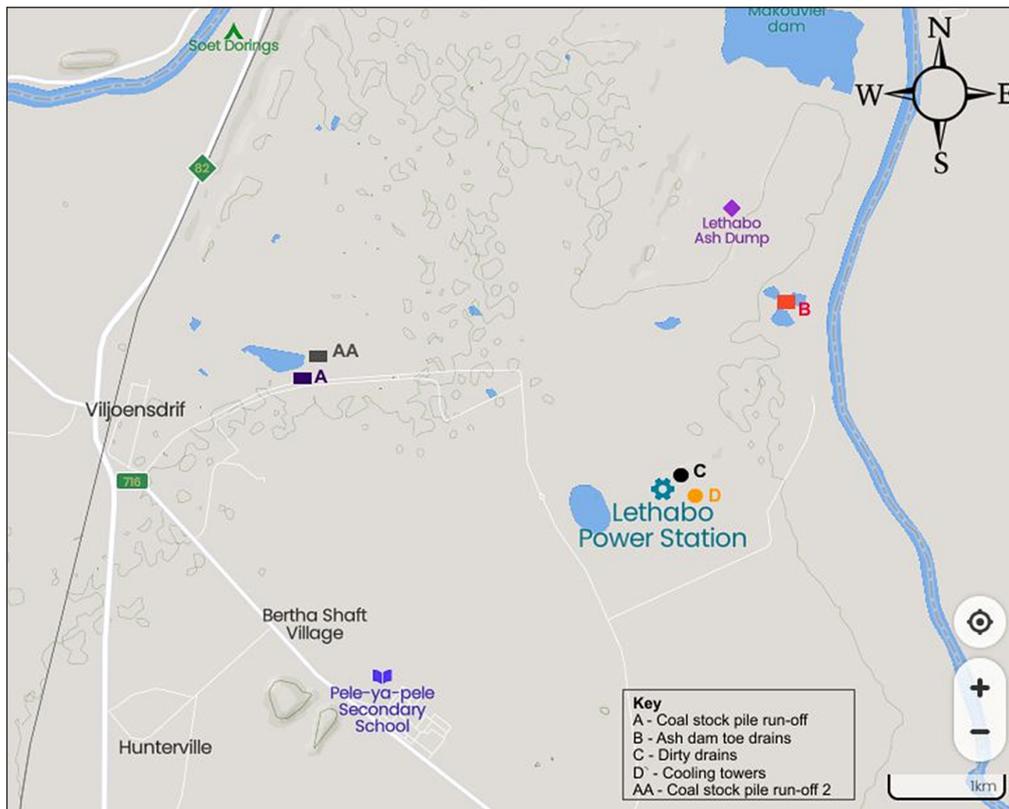


Figure 1. Sampling points were selected at Lethabo Power Station

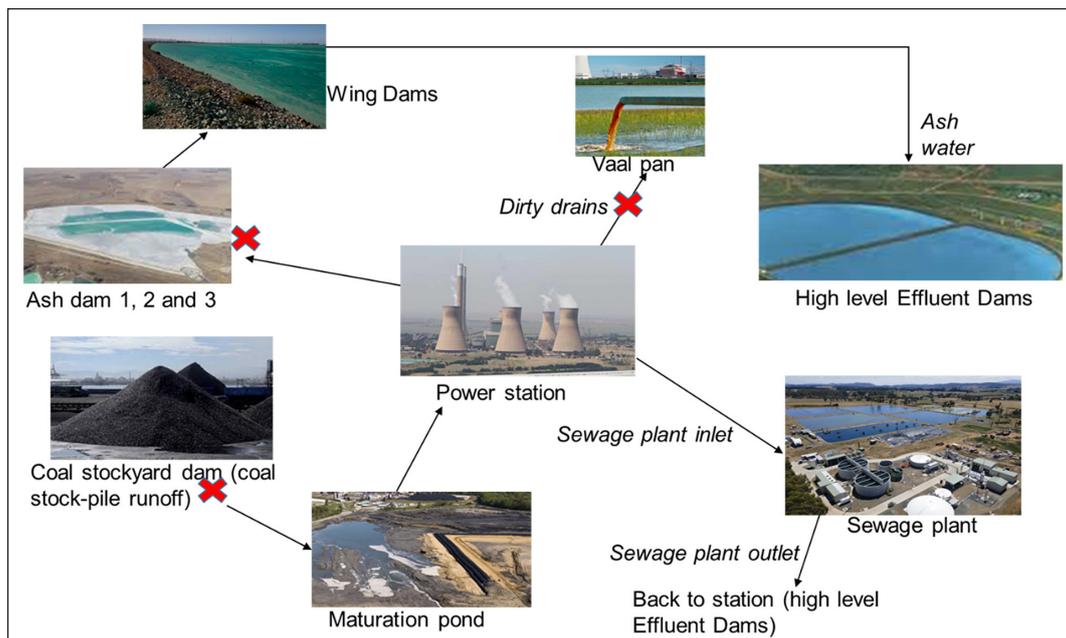


Figure 2. Sampling points (✗) were selected at Kriel Power Station

Reagents

All reagents were of high analytical purity and were used without further purification. Ultra-pure water (specific resistivity 18.2 MΩcm) was used for all dilutions and rinsing of the apparatus used in all the experiments. Sigma-Aldrich (Fluka) supplied HNO₃ (≥69%) for trace analysis. The stock solutions used to prepare standards included 1 001 µg/mL of Se and 1 000 µg/mL of yttrium (⁸⁹Y) from Specpure (Alfa Aesar, USA). The initial calibration verification (ICV) standard was prepared from a

100 mg/L Merck (Darmstadt, Germany) multi-element standard for ICP containing the analyte of interest (Se).

All solutions were stored in HDPE bottles. An acid bath (10% v/v HNO₃) was prepared for thoroughly cleaning glassware and polyethylene vials. The glassware and vials were soaked for a minimum of 12 h, rinsed several times with deionised water, followed by the final rinse with Milli-Q water, and then placed in the oven for drying at 60°C. A NIST SRM 1640a Water Reference Material (USA) was used to optimise method parameters and validate results.

Apparatus and instrumentation

Ultra-pure water was obtained from a Milli-Q Direct 8 water purification system (Millipore SAS, Molsheim, France). All glassware, microwave vessels, and centrifuge vials used were dried in a Lasec Oven Series 2000 (South Africa). An Orion pH meter (model 520A, Boston, USA) was used for pH determination in the laboratory, and an S2K712 pocket ISFET pH meter (Shindengen, Japan) was used for measuring both pH and temperature in the field. An Orion conductivity meter (manufactured by Thermo Scientific in Singapore) was used to measure electrical conductivity. Samples were filtered using Pall acrodisc membrane syringe filters, 25 mm with GxP/0.45 µm GHP (Sigma-Aldrich). A Perkin Elmer NexION 300X ICP-MS (Waltham, Massachusetts, USA) with an S10 autosampler, PolyScience 3370 chiller, and Perkin Elmer ELAN 6100 ICP-MS with AS-91 autosampler, cyclonic spray chamber, crossflow nebuliser, a kinetic energy discrimination (KED) collision cell and PolyScience recirculator/chiller (California, USA) was used for the quantitative determination of Se. The analysis of Se was conducted at KED mode and using He as an inert gas to minimise the polyatomic interferences.

Total dissolved Se analysis

Selenium was quantified using the external calibration method. As shown in Fig. 3, calibration standards were prepared. ⁸⁹Y was used as an internal standard. The ICV solution prepared was 20 µg/L, and the continuous calibration verification (CCV) was performed periodically (after every 10 samples) by analysing the midpoint concentration standard. Samples were prepared using either a 10-fold or 5-fold dilution factor. All dilutions of standards and samples were done using 1% HNO₃ prepared from HNO₃ (≥69%) and ultra-pure water. The parameters for operating the ICP-MS were set as outlined in Table 2.

Method validation

Selenium exists in trace amounts; thus, the laboratory environment, instrumentation, and materials were thoroughly cleaned. HDPE apparatus were mainly used to eliminate the adsorption of Se to the walls of the glass material and metal contaminants from the glass material. Rinsing was done several times (at least 5 times) using ultra-pure water. Apparatus were kept in clean plastic bags when not in use. The reagents used were for trace and ultra-trace analysis. Calibration standards were freshly prepared before analysis. Membrane filters were used instead of

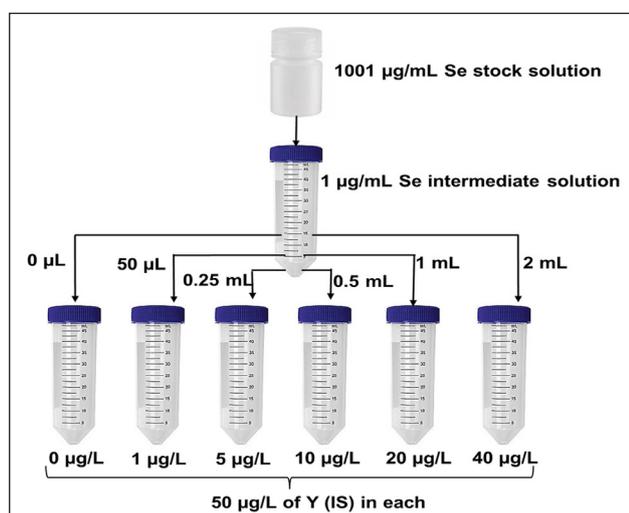


Figure 3. Preparation of a series of calibration standard solutions

ashless filter papers, which may contain trace elements at high concentrations. A NIST SRM 1640a Water Reference Material was used to validate the method. ICV and CCV were performed during the determination of total Se. The limits of detection (LOD) and quantification (LOQ) were determined by analysing 10 reagent blanks. LOD and LOQ were then calculated using the criterion based on 3 times the standard deviation of the reagent blanks and 10 times the standard deviation of the reagent blanks, respectively. Samples were prepared in triplicate to determine the precision of the results. In a few cases, samples were analysed in a different laboratory to support quality control/quality assurance (QC/QA).

RESULTS AND DISCUSSION

Physico-chemical properties

The pH values measured in the wastewater and river water samples are listed in Table 3. Generally, the wastewater pH values were 7.75–8.75, except for the Kriel ash dam toe-drain sample. The pH value for this sample was not within the South African guidelines of 5.5–9.5 for pH in effluents that can be discharged into a river (DWAF, 1995; Morrison et al., 2001). Hence, the wastewater pH has to be adjusted appropriately before discharging into the aquatic environment. The pH values in the river water samples were close to 8 and fell within the South African recommended pH range in water for domestic use (6–9) and recreation (6.5–8.5) (DWAF, 1995). Thus, based on these guidelines, the pH of the river water will not adversely affect its use for domestic or recreational purposes.

Water's electrical conductivity (EC) is a useful indicator of the water's total salt content. Salts can impact the capacity of an analytical method to qualitatively identify and quantify target elements (especially trace elements) in environmental and other samples (Zoorob et al., 1998; Bagwandin, 2016). Electrical conductivity values varied between 1 004 µS/cm and 1 806 µS/cm in wastewater from coal-fired power plants. The maximum permissible value set in the South African water quality guideline for EC in the effluent released into rivers is 1 500 µS/cm (DWAF, 1999). The Lethabo cooling towers sample exceeded this limit, and this can be expected because high evaporation takes place in the cooling towers leaving residual water with concentrated salts.

Nonetheless, the EC in wastewater from the coal-fired power plants does not appear to be a cause for concern because all the other measured values were within the acceptable limit (see Table 3).

Table 2. Optimal operating parameters for ICP-MS

| Instrument parameter | Value |
|----------------------------|---------------------------------------|
| R.F. power | *1 400–1 500 W |
| Plasma gas flow rate | *1.45–1.5 L/min |
| Auxiliary gas flow rate | No auxiliary gas |
| Lens voltage | *14 V |
| Sampling and skimmer cones | **Nickel and platinum |
| Isotopes monitored (m/z) | ⁷⁸ Se and ⁸² Se |
| Dwell time | 100 ms |
| Integration time | 2 000 ms |
| Scanning mode | Peak hopping |
| Sweeps per reading | 20 |
| Replicates | 3 |

*Optimised daily using multi-element ICP-MS tuning solution,

**cleaned before every analysis

Table 3. Physico-chemical parameters measured in the field

| Sampling area | Temperature (°C) | pH | Conductivity (µS/cm) |
|-------------------------|------------------|--------------|----------------------|
| KA | NM | 7.75 ± 0.02 | 1 420 ± 5 |
| KB | NM | 12.29 ± 0.12 | 1 501 ± 2 |
| KC | NM | 8.45 ± 0.04 | 1 223 ± 9 |
| LA | NM | 8.04 ± 0.06 | 1 011 ± 7 |
| LB | NM | 7.89 ± 0.02 | 1 458 ± 4 |
| LC | NM | 8.50 ± 0.10 | 1 344 ± 10 |
| LAA | NM | 8.21 ± 0.05 | 1 254 ± 5 |
| LD | NM | 8.16 ± 0.09 | 1 802 ± 4 |
| Olifants River influent | 21.2 | 8.45 ± 0.05 | 1 057 ± 5 |
| Olifants River effluent | 24.1 | 8.71 ± 0.15 | 1 311 ± 15 |
| Wilge River | 20.4 | 8.73 ± 0.17 | 1 217 ± 7 |

Data presented as mean ± SD, NM not measured. KA Kriel coal stockpile run-off, KB Kriel ash dam toe drains, KC Kriel dirty drains, LA Lethabo coal stockpile run-off, LB Lethabo ash dam toe drains, LC Lethabo dirty drains, LAA Lethabo coal stockpile run-off 2, LD Lethabo cooling towers.

Interestingly, secondary removal of the salts contributing to the electrical conductivity of the wastewater can be achieved if the wastewater passes through wetlands. This process would remove some dissolved salts that may have ‘survived’ the primary treatment process. The result would be much lower EC readings.

The EC in rivers in this study ranged between 1 052 µS/cm and 1 326 µS/cm. The South African acceptable limit for conductivity in the domestic water supply is 700 µS/cm (DWAf, 1996c). This limit was exceeded in the river water, which is a cause of concern because the large number of inhabitants of informal settlements along the Olifants and Wilge Rivers use the river water untreated. Although the reported EC readings are unlikely to cause imminent health effects, the water will have a noticeable salty taste. Another important observation is that the EC at Olifants River Site A (before the Duvha Power Station) was less than at Olifants River Site B (after the Duvha Power Station), an increase from 1 052 µS/cm to 1 326 µS/cm, which potentially indicates a contribution from the power plant effluent. All samples received and collected generally had values <2 000 µS/cm. Water samples with values >2 000 µS/cm may affect Se analysis if not adequately diluted because of a more complex matrix (Fernandez-Turiel et al., 2000), and this was not the case in our investigation. However, the river water’s EC may ultimately have a significantly large negative impact if consumed without treatment, particularly in areas with poor sanitation where the community uses unpurified water obtained directly from the river (for example, Masakhane village near Olifants River).

Total Se in wastewater and river waters

Over the past several decades, Se levels in wastewater and natural waters continue to be a subject of intense interest. The scientific community also recognises that speciation analysis of Se provides a more relevant indicator of the element’s potential adverse effects on the environment, because Se toxicity, reactivity, mobility, and bioavailability depend on its chemical nature. Nevertheless, determining the total Se concentration in environmental and wastewater samples is still vital. This is because most regulatory frameworks used in different regions of the world have set the upper limits for monitoring Se in terms of total concentrations (Brandt et al., 2017; Kumkrong et al., 2018). Knowledge of total Se concentration is also important because it is the foundation of speciation studies. It helps in determining accurate mass balance evaluations and provides the basis for calculating the recovery

and the ratio of the identified Se species compared to total Se (Nemeth and Dernovics, 2015; Kumkrong et al., 2018; Chen et al., 2021). This section presents the results and detailed discussions of the method developed to quantify the total dissolved Se and the application of the developed method to real samples.

ICP-MS calibration using external standard calibration technique

In this investigation, external calibration was employed. The external calibration technique is mainly recommended if the sample matrix is not complex and the differences between the matrices of the standards and the sample have no effect on the calibration function (Cuadros-Rodríguez et al., 2001; Kościelniak et al., 2011). External calibration was applicable to our study since wastewater samples were received after treatment resulting in samples with a simpler matrix. Furthermore, an internal standard described in the preceding section was used to suppress or enhance the signal arising from matrix components and the stability of instrument signal throughout the analysis. Typical regression lines (including correlation coefficient of determination and line equation) obtained during the sample analysis are indicated in Fig. 4. The correlation coefficients (R^2) of calibration curves based on 5 standards for the selected Se isotopes were in the range of 0.9993–0.9999, showing good linearity.

Internal standardisation

In ICP-MS measurements, the analytical data can be affected by suppression or enhancement of signal arising from matrix components and instrument stability throughout the sample analysis. The magnitude of the signal suppression or enhancement is known to occur regularly on the mass number, and the use of an internal standard with a mass number close to that of the analyte under investigation is recommended for correcting the effect of non-spectral interferences (Vanhaecke et al., 1992). Using an internal standard and incorporating the abovementioned criterion, improves precision and accuracy of the analytical method. The internal standard is added to each sample and standard solution before the analysis, during sample preparation (offline addition) or during analysis (online addition). The choice of the internal standard to be used depends on the task in question. An element that is selected must, ideally, be in the same average mass range as the element(s) being analysed. This selected element must not be present in the samples or should occur in the samples only

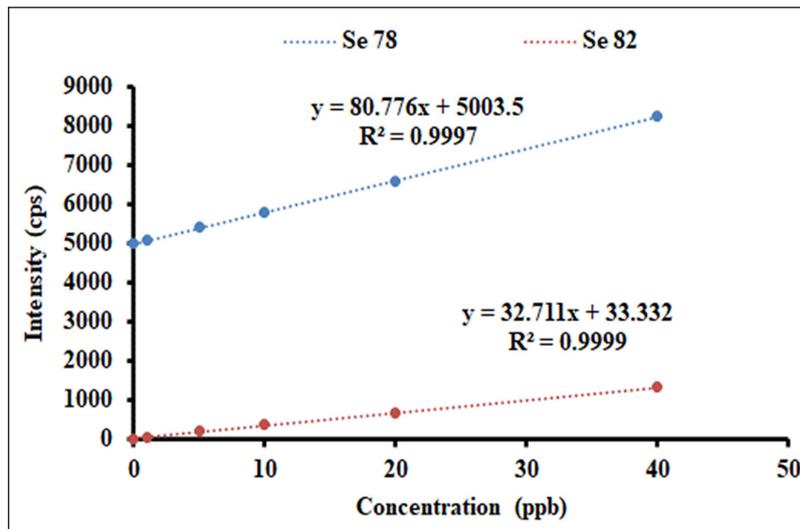


Figure 4. Typical calibration curves of Se isotopes obtained using the Perkin Elmer Elan 6100 ICP-MS

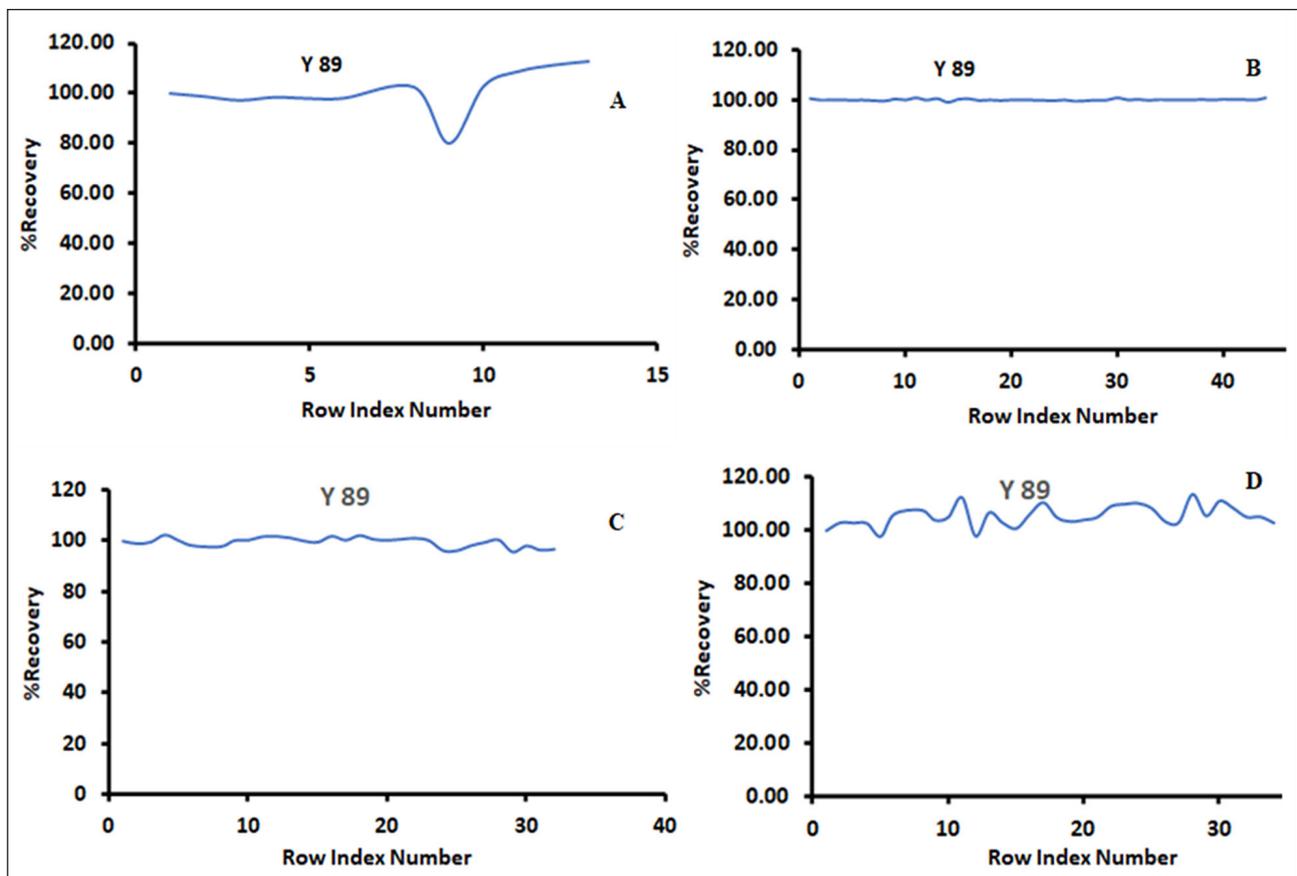


Figure 5. Variation of internal standard signal (expressed as a %) within and between analysis of the same samples

in negligible concentrations (Vanhaecke et al., 1992). ^{89}Y was selected as the internal reference standard (IRS) to correct for matrix effects, checking instrument stability, and correcting for variation of instrument response with analysis time. The selection was based on the intermediate-mass range that Se isotopes fall within. Other factors that were considered were the first ionisation potential of the IRS and analyte, interferences on the IRS, and the presence/absence of ^{89}Y in the samples. ^{72}Ge has been routinely used as an internal standard for Se analysis (Wieczorek et al., 2017; Hirtz and Günther, 2020), but the presence of Fe in the samples potentially causes interference from $^{56}\text{Fe}^{16}\text{O}^+$ [48]; hence ^{89}Y was

selected. Ideally, an internal standard should produce a stable signal throughout the analysis, but in practical situations, minor fluctuations are expected, and this was best achieved once in Fig. 5b. In other cases, the signal remained reasonably stable in standard, blank, and sample solutions (Fig. 5 a, c, and d), with a few signal fluctuations observed. The fluctuations indicated some degree of signal enhancement or suppression. Nevertheless, all the obtained recoveries were within the acceptable range, that is, between 80 and 120% (Rambla-Alegre et al., 2012). These results indicate the suitability of ^{89}Y for use as an internal standard to correct for matrix effects in the waste and natural water sample solutions.

Method validation and selection of isotopes

This research developed an ICP-MS method to determine total Se concentration in wastewater samples from coal-fired power plants and river water samples. The method was developed using certified reference material, NIST SRM 1640a Trace Elements in Natural Water. Analyses were done in triplicate to assess the precision and reproducibility of the results in terms of relative standard deviation. The LOD and LOQ used for the determination of Se are provided in Table 4, and typical correlation coefficient values of calibration curves, showing good linearity, are indicated in Fig. 4.

Ideally, the most abundant ^{80}Se should be the isotope of choice for Se analysis; however, it suffers interferences from the massive flow of the argon plasma gas. The Se isotopes that gave the best recoveries, ^{78}Se , and ^{82}Se as indicated by the results in Table 4, were selected in subsequent analysis. ^{82}Se is less abundant but has been routinely used with another less abundant isotope (^{76}Se), because these two isotopes both have less polyatomic interferences. However, ^{76}Se had a poor recovery (69%), much less than the minimum acceptable 80%, and it was apparent that ^{78}Se was the other isotope to be used. It can be argued that ^{78}Se is subject to strong interference by $^{40}\text{Ar}^{38}\text{Ar}^+$ and $^{38}\text{Ar}^{40}\text{Ca}^+$, each at $m/z = 78$ (May et al., 1998), but $^{40}\text{Ar}^{38}\text{Ar}^+$ interference can also be corrected by blank subtraction because it is stable and independent of individual samples. ^{38}Ar also has an abundance of 0.0629%, which is relatively low. This generally means that the sensitivity of ^{38}Ar polyatomic interference will be very low given the above relative abundance. For these reasons, ^{78}Se has also been routinely used to analyse water samples (Smith and Compton, 2004; Pettine et al., 2015; Kleckner et al., 2017). Thus, using ^{78}Se and ^{82}Se , the standard reference material (SRM) 1640a, percentage recoveries ranged

from 92% to 96%, with RSDs below 4%, which were both within the acceptable ranges. The method detection limit was 0.13 $\mu\text{g/L}$, and the limit of quantity was 1.84 $\mu\text{g/L}$. These values are relatively low compared to the literature values (0.064–7 $\mu\text{g/L}$) reviewed by Kumkrong et al (2018), which indicated that our developed method could be used for routine analysis of Se in water samples.

Analysis of real samples

The developed method for the total determination of Se was applied to wastewater and natural water samples. All samples were analysed in triplicate ($n = 3$) to evaluate precision (%RSD), and the reported results are mean concentrations. After all corrections by the internal standard (^{89}Y), the concentration value of Se in a given sample must be higher than LOQ for it to be acceptable. This criterion was not met for Kriel ash dam toe-drains, Kriel dirty drains, Lethabo dirty drains, and Olifants River influent samples. The two Se isotopes selected for this method also showed similar results. The results are presented in Table 5. The total Se concentrations were generally less than 10 $\mu\text{g/L}$.

The total Se concentrations in natural waters, according to global reports, were reported to range from 0.1–400 $\mu\text{g/L}$ [53], and it can be seen that the measured concentrations in the selected rivers and dams fall in the lower boundary of this range. There is a slight increase from the Olifants River Site A (undetectable concentrations) to the Olifants River Site B (detectable concentrations). This slight rise can be attributed to the Duvha coal-fired power plant, which is close to the river. The rise is greater than 2 $\mu\text{g/L}$ and exceeds the stipulated freshwater value for aquatic life limit of 2 $\mu\text{g/L}$ (Kumkrong et al., 2018). This rise in Se concentrations is a cause of concern for aquatic life, and a practical solution is required from the power station.

Table 4. Validation of method and selection of isotopes using SRM 1640a

| Isotopes | LOD ($\mu\text{g/L}$) | LOQ ($\mu\text{g/L}$) | Measured ($\mu\text{g/L}$) | Certified values ($\mu\text{g/L}$) | % Recovery |
|------------------|-------------------------|-------------------------|------------------------------|--------------------------------------|------------|
| ^{74}Se | 0.219 | 0.731 | 14.6 \pm 3.0 | 20.13 \pm 0.17 | 73 |
| ^{76}Se | 0.535 | 1.784 | 13.8 \pm 1.3 | 20.13 \pm 0.17 | 69 |
| ^{77}Se | 1.491 | 4.97 | 29.8 \pm 1.1 | 20.13 \pm 0.17 | 145 |
| ^{78}Se | 0.129 | 0.429 | 19.1 \pm 0.7 | 20.13 \pm 0.17 | 96 |
| ^{80}Se | 2.78 | 9.28 | 32.8 \pm 2.1 | 20.13 \pm 0.17 | 160 |
| ^{82}Se | 0.553 | 1.84 | 18.3 \pm 0.9 | 20.13 \pm 0.17 | 92 |

Data presented as mean \pm S.D

Table 5. Total Se concentration in waste and river water

| Sample name | Concentration ($\mu\text{g/L}$) | |
|--------------------------------------|-----------------------------------|------------------|
| | ^{78}Se | ^{82}Se |
| ^a KA | 7.67 \pm 0.52 | 7.17 \pm 0.63 |
| ^a KB | <0.129 | <0.553 |
| ^a KC | <0.129 | <0.553 |
| ^a LA | 6.62 \pm 0.42 | 5.73 \pm 0.56 |
| ^a LB | <0.129 | <0.553 |
| ^a LC | 8.23 \pm 0.30 | 6.92 \pm 0.11 |
| ^a LAA | 5.03 \pm 0.17 | 5.12 \pm 0.21 |
| ^a LD | 5.48 \pm 1.59 | 5.18 \pm 0.19 |
| ^b Olifants River influent | <0.129 | <0.553 |
| ^b Olifants River effluent | 3.67 \pm 0.50 | 3.10 \pm 0.06 |
| ^b Wilge River | 7.98 \pm 0.22 | 6.73 \pm 0.05 |

Data presented as mean \pm SD, ^aSamples analysed using NexION 300X ICP-MS, ^bSamples analysed using Elan 6100 ICP-MS. Sampling points are named as in Table 3.

The wastewater from coal-fired power plants in the USA, Canada, Europe, and China contains Se in concentrations ranging from 1–10 mg/L, particularly the flue-gas-desulfurisation (FGD) wastewater (Santos et al., 2015). The values obtained in this study were far less than this range. The South African coal-fired power plants utilise pulse jet fabric filters (FFs) or electrostatic precipitators (ESPs) and flue gas conditioning (FGCs) systems to trap the flue gas pollutants (mainly SO_x). These systems are not efficient in trapping volatile trace elements such as Se and As (Dabrowski et al., 2008; Shah et al., 2008; Tian et al., 2021). Thus, Se may escape into the atmosphere resulting in low Se concentration in the generated coal-fired power plant wastewater. The quantity of Se in the wastewaters from coal-fired power plants can vary depending on the type of coal used. Wagner and Tlotleng (2012) determined the average Se concentrations to be 0.99 ± 0.24 µg/g in South African coal, implying lower concentrations in wastewaters owing to losses during the cleaning of the coal and other processes (for example, leaching and percolation during storage). However, in this investigation another major reason for the low concentrations obtained is that the wastewater samples were received after treatment.

CONCLUSION

A method for determining Se in wastewater samples from coal-fired power plants and natural (river) waters located near the power stations was successfully developed using ICP-MS. The method requires the least sample preparation and has competitive LOD (0.13 µg/L) and LOQ (1.84 µg/L); thus, it can be routinely used for Se analysis in water samples. ⁷⁸Se and ⁸²Se give more accurate and precise results when analysing the water samples using ICP-MS in standard mode and ⁸⁹Y is a suitable IRS that can be substituted for ⁷²Ge in Se analysis. The Se concentrations obtained in real samples do not exceed the stipulated South African Se hazard index for drinking water, water for livestock, water for human consumption, and irrigation. However, the treated wastewater is unsuitable for discharge in river/surface water because Se concentration exceeds the limit for freshwater for aquatic life. The slight increase of Se concentration from the Olifants River Site A to the Olifants River Site B can be attributed to the Duvha coal-fired power plant in proximity to the river. This increase poses a threat to aquatic life in the Olifants River but is of minor concern for humans, livestock, and irrigation. There may be a cause of concern for Se deficiency because Se is essential at low concentrations, i.e. ~ 50 µg/L per day. South African coal-fired power plants need to improve and incorporate wastewater treatment technologies that efficiently remove Se to comply with all regulatory frameworks gazetted for Se.

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