Pre-concentration and determination of traces of nitrobenzene and 1,3-dinitrobenzene in water samples using anthracite adsorbent

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This study introduces a novel analytical method for the determination of nitrobenzene (NB) and 1,3-dinitrobenzene (DNB) from an aqueous solution using high performance liquid chromatography (HPLC) and anthracite as adsorbent for pre-concentration. The method showed good linearity for determination of NB and DNB concentrations in the range of 0.10–200 µg L⁻¹ with regression coefficients better than 0.9995. Limits of detections (LOD) were 0.010 and 0.055 µg L⁻¹ for DNB and NB, respectively. Relative standard deviations (RSD) for 0.50 µg L⁻¹ and 150 µg L⁻¹ were in the range of 2.0–3.8% for (DNB) and 3.0–4.8% for (NB).

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1. Introduction

In many parts of the world and in particular in third-world countries diseases and health problems have often been caused by discharging untreated or inadequately treated wastewater. Water polluted with toxic compounds has serious negative impact on all living creatures and water used for drinking, household consumption, recreation, fishing, transportation, agriculture and commerce. So, the determination of trace amounts of organic pollutants in water samples has been one of the major challenges in the last few decades. Nitrobenzenes as carcinogenic pollutants are member of persistent organic pollutants (POPs) and show particular characteristics such as toxicity and persistance within ecosystems [1–5]. Nitrobenzene (NB) is an important organic material and has been widely adopted in the manufacture of intermediates in chemical synthesis industries for producing raw materials such as aniline, quinoline, azobenzene and trinitrotoluene. These compounds are used in making explosive materials, rubber, pesticides, agricultural chemicals and solvents for coating materials and dyes. Many studies have reported that NB is ubiquitous in the environment and organisms in many animals and humans [6–8]. Main contamination sources of surface and waste waters by NB are oil spills, industrial and municipal discharges and air input [6,9]. A large proportion of NB which is generally discharged into wastewater treatment plants is difficult to remove by conventional treatment processes and causes more pollution in the surrounding aquatic environment [10,11]. The high eco-toxic and ubiquitous character of NB and its derivatives are potential threats to the ecosystem and human health [12,13]. Environmental protection agencies (EPAs) in many countries regard NB as a “pollutant of main concern” [6,13] and have been classified as one of the 129 priority pollutants by the United States environmental protection agency (USEPA) [14,15]. Some aromatic compounds such as NB remain in the environment for relatively long periods of time. The half-life of NB in the atmosphere is approximately 4 months [16]. The above-mentioned hazard characteristics of NB and its derivatives are a challenging problem to devote more attention on determining and monitoring these hazardous compounds in aqueous environments.

Several diverse methods were applied for the determination of nitrobenzenes in environmental samples. Amongst these are ultraviolet spectrophotometry (UV) [17], fluorescence quenching [18–20], high performance liquid chromatography (HPLC) [21–25], gas chromatography (GC) [26–31], capillary electrophoresis (CE) [32] and electrochemical methods [33–40]. Some of these techniques suffer from interferences and matrices. On the other hand, low level of these constituents makes their determination a difficult task.

Solid-phase extraction (SPE) is superior to other extraction methods like liquid–liquid extraction (LLE) in different terms such as higher selectivity, extractability, reproducibility without emulsion formation. Different synthetic and natural SPE adsorbents (such as C18 materials, nanoparticles, zeolite resins, silica, activated carbon and clays) are used for separation of toxic

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compounds [17,22,23,31]. Some of these adsorbents suffer from multistep treatment and modification processes. Therefore, it would be beneficial to find, develop and design new SPE adsorbents that require minimum treatment steps [41,42].

Anthracite (ANTC) is a hard and compact type of mineral coal that has a high luster and also high carbon content. It has fewest impurities and bituminous coal and lignite. ANTC is the most metamorphosed type of coal with a carbon content of between 92.1% and 98% and low percentage of volatile matter. ANTC has a relative density of 1.3–1.4 g cm\(^{-3}\) and luster that is often semi-metallic with a mildly brown reflection. ANTC abundantly appear in areas of considerable earth-movements such as the flanks of great mountain ranges. However, few articles are published about adsorptive properties of ANTC to remove and adsorb toxic substances [43,44].

Geochemical studies show the presence of many aliphatic and aromatic hydrocarbons in coal. Most coal consists of mechanical mixture of two principal organic components: (1) resin-like (aliphatic) organic matter of uncertain origin (that is, specific plant structures that have been destroyed during the coalification process) and (2) benzene-like (aromatic) organic matter derived from wood tissue (lignin). Different analytical techniques and instruments such as gas chromatography/mass spectrometry, the electron microscopy and the scanning electron microscopy are used to study the concentration and distribution of organic compounds in coals [45].

Herein, a new procedure was introduced for highly efficient solid phase extraction (SPE) and pre-concentration of nitrobenzene (NB) and 1,3-dinitrobenzene (DNB) from water samples by using ANTC adsorbent particles. The proposed method demonstrated the high potential ability of ANTC particles to separate ultra-trace concentrations of NB and DNB with a high level of efficiencies. The pre-concentrated target analytes (NB and DNB) were successfully evaluated by HPLC following elution by an efficient desorbing solvent. The proposed method has high potential applicability for the determination of ultra trace amounts of NB and DNB in water samples.

2. Experimental

2.1. Chemicals and reagents

All chemicals and reagents were of analytical grade. Acetone (99.5%, w/w), acetonitrile (HPLC grade), water (HPLC grade), nitrobenzene (NB) and 1,3-dinitrobenzene (DNB) were purchased from Merck (Darmstadt, Germany) and used without further purification. Anthracite particles (purity 97%, specific surface area ≤4 m\(^2\) g\(^{-1}\), average particle size of ≥5 μm) were obtained from Kimia Teb (Ahvaz, Iran). Stock solutions (100 mg L\(^{-1}\)) for NB and DNB were prepared by dissolving 100 mg of each compound in water–acetonitrile (70:30) solution mixture and dilution to the mark in 1000 mL volumetric flask. Other concentrations were prepared by successive dilution the stock solutions with double distilled water.

2.2. Apparatus

Chromatographic measurements were carried out using a Knauer HPLC system (Germany) consisting of a K-1001 pump and a k-2501 UV detector. A pH-meter (827 pH lab, Metrohm\(^{®}\), Herisau, Switzerland) was also used for pH adjustment. Infrared spectrum was obtained using a Fourier Transform-Infrared Spectrometer (FT-IR spectrum 100, Perkin Elmer, Australia) to identify functional groups and chemical bonding of ANTC and DNB@ANTC. Scanning electron microscopy (SEM) analysis was made using Hitachi S-4500 SEM (Japan) at 20 kV to measure size and shape of particles. Structural analysis of the ANTC was made using an X-ray diffractometer (XRD, Brucker D8 Discover, Germany).

2.3. Pretreatment of ANTC adsorbent

A pretreatment step was applied to increase adsorption efficiency of the adsorbent and to prevent extraction of organic compounds from the matrix of ANTC [45]. The pretreatment step is as follows: 50 g of micro-sized ANTC was added to 500 mL pure water and boiled for 1 h and subsequently allowed to settle down for 5 min. The clear supernatant was decanted and ANTC particles were transferred to an oven and dried at 200 °C for 6 h and stored in a sealed bottle for further uses.

2.4. Extraction procedure

The extraction procedure consisted of the following steps. At the first step, 25 mL of the sample solution at pH 4 was added to 100 mL beaker containing 0.25 g of pretreated ANTC and the mixture was stirred for 6 min (200 rpm). Then, the adsorbent was isolated from the sample solution by decanting the clear supernatant and the ANTC settled down due to its high density (d = 1.3–1.4 g cm\(^{-3}\)) without centrifugation or filtration. The isolated adsorbent particles remained in the beaker and were washed with 2 mL of distilled water and then 0.5 mL of pure acetonitrile was added to assist the desorption of DNB and NB from the adsorbent surface. After 1 min the adsorbent particles were heated on a hotplate at 45 °C to dryness and evaporation of acetone. Solubility of both NB and DNB in acetone is better than water and can help the desorption process. But, acetone absorbs strongly at 275 nm in the UV region which can interfere with the determination of both NB and DNB. To prevent the interference of acetone, evaporation of this solvent must be carried out before the determination of NB and DNB. Analytes were finally desorbed by 0.5 mL of HPLC grade acetonitrile after a contact time of 6 min with the adsorbent. 20 μL of desorbing solvent containing NB and DNB was suctioned by a HPLC syringe and used for further HPLC analysis.

2.5. HPLC analysis

A Nucleodur (100-5 C\(_{18}\), 250 mm × 4 mm) column, acetonitrile/water at the ratio of 70:30 as the mobile phase (isocratic) and a 20 μL injection loop were used. The temperature of the column oven was kept constant to 25 °C, while the mobile phase flow rate fixed at 1.0 mL min\(^{-1}\). Under these conditions, chromatographic retention times for DNB and NB were 4.1 min and 4.6 min, respectively. The detection wavelength for DNB and NB was set at 254 nm.

3. Results and discussion

3.1. Characterization of the anthracite adsorbent

The XRD pattern (Fig. 1A) with broad reflections in the range of 20–30 °C show amorphous structure of anthracite. Graphitic structures developed in the anthracite sample (2θ of 26.5, 44.7). XRD profiles show the dominance of disorganized amorphous carbon in the samples. FT-IR studies used to identify ANTC functional groups and also chemical bonding of those compounds attaching to it. Scanning electron microscopy (SEM) was used to observe the surface physical morphology and determine the size of ANTC and DNB@ANTC particles. Fig. 1B shows the structure of ANTC before the adsorption process without any pretreatment and Fig. 1C indicates the ANTC adsorbent after adsorption of DNB. It is
noteworthy that because of the low amount of adsorbed DNB onto ANTC surface no significant difference was observed in the SEMs before and after adsorption of DNB.

FT-IR spectra (Fig. 2a–c) show characteristic peaks of ANTC (a), DNB (b) and DNB@ANTC (c). The peaks at 1000–1100 cm\(^{-1}\) were assigned to C–O and C–O–C stretching and others at 1650–1450 cm\(^{-1}\) were assigned to aromatics C=C stretching. The stretching of C=O at 1640 cm\(^{-1}\) in the anthracite spectra shows the presence of carbonyl group (Fig. 2a). Conjugated or dissubstituted unsaturated carbon bonds confirmed by the presence of the peaks at 2400–2300 cm\(^{-1}\) [46]. Fig. 2b shows the FT-IR spectra of DNB with characteristic N=O peaks at 1538 and 1347 cm\(^{-1}\). The pattern of the out-of-plane C–H bending bands in the region of 900–675 cm\(^{-1}\) and the =C–H stretch at 3100–3000 cm\(^{-1}\) are characteristics of this aromatic compound. FT-IR of DNB@ANTC (Fig. 2c) demonstrates the characteristic peaks of both ANTC and DNB that strongly support the adsorption of DNB on ANTC as an adsorbent.

The physisorption of aromatics on the surface of carbon based adsorbents takes place mainly throughdispersive interactions between the aromatic molecules and the carbon basal planes. One of the most important adsorption mechanisms involves the interaction between the delocalized \(\pi\) electron of the carbon surface and the free electrons of the rings of aromatic molecule. These dispersive interactions are basically in the form of van der Waals interactions. The heterogeneous oxygen groups attract and localize the electrons of the basal planes, hence, forming partially positive 'islands' in the basal planes. On the other hand the functional group attached to the aromatic adsorbate can activate or deactivate the benzene ring to which it is attached. Electron donor groups which create partially negative benzene ring by pushing the electrons toward the ring are well known as activators. Deactivating groups attract the electrons and produce a partially positive ring. Since the benzene ring has a larger size compared to the functional group, the interaction of the benzene ring with the surface basal planes is more effective in the adsorption mecha-

![Fig. 1. (A) XRD pattern of ANTC, (B) SEM of ANTC and (C) SEM of DNB@ANTC.](image)

![Fig. 2. FT-IR spectrum of ANTC (a), DNB (b) and DNB@ANTC (c).](image)
Nitrobenzene is a compound with a deactivating group (−NO₂) that does not form H-bonding. According to the results reported by Franz et al. [47], water adsorption is dominant due to H-bondings in alkaline aqueous solution of NB and this should cause the adsorption capacity to decrease for nitrobenzene as the amount of surface oxygen groups is increased. In the high pH solutions, hydroxyl groups on the carbon surface dominate and cause an increase in the adsorption of water molecules and cause a decrease in the adsorption of nitro-aromatic compounds. In moderate acidic solutions the adsorption of nitro-aromatic compounds will increase [47,48].

3.2. Effect of pH

The effect of sample solution pH in the range of 3–9 on the recovery of target analytes (NB and DNB) was studied. The pH of test solution (25 mL, 25 μg L⁻¹ of NB and DNB solution mixture) was adjusted to the desired value using diluted solutions of 0.1 M HCl or 0.1 M NaOH. The extraction procedure was followed as Section 2.4. Results showed that the maximum recovery was obtained at pH 4. As mentioned in the previous section, mild acidic solution will assist the adsorption of NB and DNB on the ANTC surface.

3.3. Effect of the amount of ANTC

Different amounts of ANTC in the range of 0.05–0.40 g were used for the adsorption/desorption of NB and DNB from water sample. As shown (Fig. 3) the recovery rate increased for ANTC amounts up to 0.25 g. For amounts more than 0.25 g of ANTC recoveries decreased because of incomplete desorption of analytes from adsorbent surfaces due to the small volume of acetonitrile (0.5 mL) as the desorbing solvent. Using 0.25 g of ANTC as the optimum amount made possible quantitative adsorption of analytes. More than 75% recovery of analytes for 25 mL sample solution containing NB and DNB (25 μg L⁻¹ of each component) was achieved at this amount of ANTC. Different tests proved that this amounts of ANTC (0.25 g) can be used for pre-concentration of analytes concentration up to 200 μg L⁻¹ for each component in the solution mixture.

3.4. Effect of contact time

Different contact times from 2 to 11 min were investigated for pre-concentration of NB and DNB (25 ng mL⁻¹ of each component) form water samples and results are shown in Fig. 4. It was found that contact time of 6 min at stirring speed of 200 rpm was enough for the effective extraction of NB and DNB from 25 mL sample solutions and effective desorption of both analytes from the ANTC particles. It must be mentioned that for larger solution volumes (up to 200 mL), a contact time of 6 min was enough for the nearby complete adsorption of NB and DNB with a fixed amount (0.25 g) of ANTC. Contact times longer than 6 min decreased the recovery rates (specially NB) which may be due to the stirring hydrodynamic forces that affect the weak interaction between the adsorbent surface and analytes that accelerate back diffusion of NB to water that emerged high solubility of NB in water [12].

3.5. Desorption of NB and DNB from ANTC

Different solvents including methanol, n-hexane and acetonitrile were tested to determine the best solvent composition for effective elution of analytes. Selections of these desorbing solvents were made according to their potential to release both analytes from the surface of ANTC particles. Results showed that recovery for pure methanol is 9.5%; pure n-hexane 18%; pure acetonitrile 76%; methanol–n-hexane (50:50) 13%; methanol–acetonitrile (50:50) 40% and n-hexane–acetonitrile (50:50) 53%. It must be mentioned that washing the adsorbent particles with 0.5 mL of acetone and then heating the adsorbent particles until dryness on a hotplate at 45 °C, was effective for quantitative elution and desorption of both target analytes from the pores of the ANTC. Finally, desorption of analytes (NB and DNB) was carried out using 0.5 mL of pure acetonitrile which showed highest elution ability among the tested solvents. It must be mentioned that desorption time between the desorbing solvent and ANTC particles affected
Effect of ionic strength

The effect of ionic strength on adsorption and pre-concentration processes was examined using different concentrations of NaCl as electrolyte. Results show that adsorption and extraction efficiencies of NB and DNB were increased by increasing the NaCl concentration up to 0.1 M of NaCl but peak areas of both analytes decreased slightly in more concentrated (up to 0.5 M) solutions due to the saturation of active adsorbent sites by co-existing ions. This implied that electrostatic attraction did not play a significant role in the adsorption/desorption steps under these test conditions.

Effect of co-existing species

The effects of co-existing ions and molecules such as Na⁺, Cl⁻, Al³⁺, CO₃²⁻, SO₄²⁻, SCN⁻, NO₂⁻, HCO₃⁻, Mg²⁺, Mn²⁺, HPO₄²⁻, C₆O₃²⁻, CH₃COO⁻, citrate and aromatic compounds including phenol, benzene, naphthalene, phenanthrene and anthracene as most common species in water samples were investigated using optimum experimental conditions. The pre-concentration and desorption of NB and DNB (25 μg L⁻¹ of each component) from the solution mixture were done in the presence of co-existing ions and some aromatic compounds. The maximum acceptable error was determined as ±5%. Results showed that these species did not interfere with the pre-concentration and desorption and subsequent determination of analyte process even at high concentration ratios (tolerable concentration ratio >2000) for inorganic ions and phenol, tolerable concentration ratio >1800 for benzene and tolerable concentration ratio >40 for naphthalene, phenanthrene and anthracene) with respect to NB and DNB. These results show that most ions and organic molecules do not affect adsorption and extraction processes.

Breakthrough volume

The effect of sample volume on adsorption and pre-concentration processes was investigated using a series of solutions with fixed amounts of NB and DNB (625 ng of each) at different volumes. Results show that initial sample volume had no effect on the recovery rate up to 150 mL and recoveries ≥93% were obtained for sample volumes up to 150 mL. Enrichment of analytes to 0.5 mL acetonitrile make possible to obtain a pre-concentration factor of about 300.

Adsorption isotherm

The capacity of ANTC used for the removal of NB and DNB was examined by measuring the initial and final concentrations of two components in the test solution (pH 4, 25 °C and contact time of 10 min) in a batch system. Different test solutions with NB and DNB concentrations in the range of 1–100 μg L⁻¹ were examined with a fixed amount of ANTC (0.40 g). Both Langmuir and Freundlich adsorption isotherms were used to normalize the adsorption data. The results showed that Langmuir model fitted better (R₂ NB = 0.9932, R₂ DNB = 0.9914) than the Freundlich model (R₂ NB = 0.9601, R₂ DNB = 0.9468). These results support the view that the adsorption of NB and DNB onto ANTC occur through a monolayer pattern via physical adsorption between the carbon content of ANTC. The Langmuir isotherm equation was used to describe the relationship between the amount of component adsorbed and its equilibrium concentration in solutions.

\[
\frac{C}{q} = \frac{1}{K_{eq} m} + \frac{C}{q_m}
\]

where C (mg L⁻¹) is the equilibrium concentration of one of the NB and DNB in the solution, q (mg of adsorbate per g of adsorbent) is the equilibrium adsorption amount of NB and DNB, q_m is the maximum adsorption amount of analyte per gram of adsorbent (mg g⁻¹) and K is the Langmuir adsorption equilibrium constant in liter per mg of adsorbent (L mg⁻¹).

The linear relationship between C/q and C shows the applicability of the Langmuir model:

\[
\text{NB}: \ y = 1.7332x + 0.2349 \quad (R^2_{\text{NB}} = 0.9932)
\]

\[
\text{DNB}: \ y = 1.4883x + 0.1285 \quad (R^2_{\text{DNB}} = 0.9914)
\]

The K values were 7.38 and 11.58 (as Langmuir adsorption equilibrium constant, L mg⁻¹) and q_m values were 0.577 and 0.672, (as the maximum adsorption amounts of analyte per gram of adsorbent, mg g⁻¹) for NB and DNB, respectively.

Reusability of the ANTC adsorbent

Tests were done on potential reusability of the adsorbent in several successive adsorption and desorption processes and used ANTC was washed by acetone and water after each desorbing cycle. Results of these tests showed that this adsorbent could be reused effectively three times without any considerable loss of adsorption efficiency (RSD < 5%) (Fig. 6).

Analytical characteristics

Calibration curves for NB and DNB were obtained in the concentration range of 0.10–200 μg L⁻¹ (n = 10) after pre-concentration with ANTC and desorption with 0.5 mL acetonitrile. The equations are y = 3768x + 38.25 for DNB and y = 3406.8x – 407 for NB, where y is the peak area and x is the analyte concentration in μg L⁻¹. Good correlation coefficients (R = 0.9998) and high linear range for both analytes were achieved. These relations between NB and DNB peak areas to their initial concentrations were applied for subsequent calculations. The repeatability of the method in terms of relative standard deviation (RSD, %) was evaluated for 0.50 and 150 μg L⁻¹ solutions (n = 6) of NB and DNB and it was found that RSD values were in the range of 3.0–4.8% for NB and 2.0–3.8% for DNB. The interday precision was measured in five days with three
repetitions each day. The average recoveries for DNB and NB were 86–107% and 80–108%, respectively, with the intraday relative standard deviations (RSDs) of 2.4–4.6% and 3.3–5.2%, respectively. The interday RSDs were 3.0–4.7% for DNB and were 3.7–5.4% for NB.

Limits of detections (LODs) based on signal/noise = 3 of the method were 0.010 μg L⁻¹ for DNB and 0.055 μg L⁻¹ for NB and limits of quantifications (LOQs) based on signal/noise = 10 were 0.1 μg L⁻¹ for both analytes. An enrichment factor of 300 was obtained for NB and DNB by comparing the maximum sample volume without breakthrough (150 mL) and the desorbing volume of acetonitrile (0.5 mL). The average desorption recoveries for NB and DNB were 80% and 87%, respectively, that satisfy with the 70–130% recoveries range criterion [49].

3.12. Analysis of the raw river water

To determine the ability of the proposed method for NB and DNB analysis in a real sample, raw water from the Karon river water was tested and spiked. A simple clean-up step was carried out as follows: 25 mL of water sample was filtered through a Whatman 42 filter paper and recommended procedure was applied. No chromatographic signal of target analytes in the pretreated sample solution was observed. Standard addition method was applied to estimate the reliability of the proposed method. In this regard, different amounts of NB and DNB were added into the river raw water samples and described procedure was undertaken and analytical results are summarized in Table 1. The proposed method indicated satisfactory recoveries for NB and DNB determination in real samples. This revealed that the proposed method is applicable for target analytes sensing for direct analysis of NB and DNB in surface water samples. Evaluations indicated satisfactory recoveries and support high selectivity that cause the matrix of raw water sample does not interfere with pre-concentration and determination of ultra trace amounts of NB and DNB.

4. Conclusions

ANTC has been used successfully for simultaneous adsorption and pre-concentration of NB and DNB in aqueous solutions. The proposed SPE procedure offered high enrichment factors and effective pre-concentration in a relatively short time. This method showed advantages including reusability of anharmonic microparticles, simplicity, wide linear range and low detection limit. The method demonstrated very good efficiencies in moderate salt concentration (0.1 M NaCl). The method could extract and determine ultra trace levels of NB and DNB (0.1 μg L⁻¹) in a short analysis time (about 15 min). It also showed much better LODs and comparable LOQ, RSD and recovery rates in comparison to a variety of other methods reported in related literature for the determination of related compounds (Table 2).

Acknowledgement

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Table 1

<table>
<thead>
<tr>
<th>Conc. added to river water (μg L⁻¹)</th>
<th>Conc. quantified (μg L⁻¹)</th>
<th>%Recovery (RSD)</th>
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<tbody>
<tr>
<td>Raw water</td>
<td>&lt;DL (DNB), (NB)</td>
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<tr>
<td>Raw water 0.50 (NB, DNB)</td>
<td>0.39 (DNB), 0.60 (NB)</td>
<td>77.0 (3.6), 120.0 (3.9)</td>
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<tr>
<td>Raw water 1.0 (NB, DNB)</td>
<td>1.02 (DNB), 1.00 (NB)</td>
<td>102.0 (3.2), 100.5 (4.1)</td>
</tr>
</tbody>
</table>

Table 2

Comparison of the analytical performance of the different reported methods for NB quantification.

<table>
<thead>
<tr>
<th>Method</th>
<th>LDRa (μg L⁻¹)</th>
<th>LODb (μg L⁻¹)</th>
<th>RSD</th>
<th>Ref.</th>
</tr>
</thead>
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<tr>
<td>Electrochem.</td>
<td>123–24,600</td>
<td>6</td>
<td>-</td>
<td>[40]</td>
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<tr>
<td>Electrochem.</td>
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<td>-</td>
<td>[39]</td>
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<td>[38]</td>
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<td>[35]</td>
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<td>-</td>
<td>[29]</td>
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<td>0.006 (NB)</td>
<td>3.3–4.8</td>
<td>This work</td>
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</table>

a Linear dynamic range.

b Limit of detection.