Journal of Chemical Technology and Metallurgy, 61, 1, 2026, 83-92

OPTIMIZATION OF THE EXTRACTION CONDITIONS FOR THE Hg^{2+} - DITHIZONE COMPLEX IN CHLOROFORM AND ITS DETERMINATION BY UV-VIS SPECTROPHOTOMETRY

Veronika Ivanova, Kristina Minkova, Kalin Chakarov

University of Chemical Technology and Metallurgy
8 Kliment Ohridski Blvd., Sofia 1797, Bulgaria, veronika@uctm.edu (V.I.);
kristina_minkova@abv.bg (K.M.); chakarov@uctm.edu (K.Ch.)

Received 30 October 2025
Accepted 20 November 2025
DOI: 10.59957/jctm.v61.i1.2026.8

ABSTRACT

This study aimed to optimize a UV - Vis spectrophotometric method for determining mercury based on its extraction with dithizone in chloroform. In the present work, the effects of pH, reagent concentration, stoichiometry of the complex were investigated. In addition, the sensitivity of the method was determined by calculating the molar absorbance, assessing the linearity and shaking time. Optimal conditions were established at pH ≈ 1.0 ± 0.1, using 4.00 mL of 5.00 mg L^{-1} dithizone and 1.00 min shaking. Under these parameters, the method showed stable absorbance and reproducible results. The calibration was linear within 0.80 - 1.10 mg L^{-1} Hg, and recovery tests yielded 71 - 74 % for spiked tap and deionized water samples. The optimized procedure provides reliable preliminary mercury determination and can be further adapted for complex matrices such as sediment, soil, or coal after microwave digestion.

Keywords: mercury, UV-Vis, Hg^{2+}- dithizone complex, liquid-liquid extraction, optimization.

INTRODUCTION

Mercury (Hg) is one of the most toxic and persistent trace elements in the environment. It can exist in several oxidation states and forms stable complexes with sulfur-containing compounds. Due to its volatility, ability to travel long distances in the atmosphere, and tendency to bind to solid particles, mercury is found in almost every component of the environment, such as air, water, soil, and sediments. Once in aquatic systems, it redistributes between the dissolved and particulate phases. Moreover, it accumulates in sediments and can re-enter the water column under changing redox or pH conditions [1 - 3]. Sediments therefore act as both a sink and a potential secondary source of mercury, reflecting historical and current contamination. contamination [4].

Globally, the monitoring of mercury in aquatic environments remains a priority under the Minamata Convention [5]. In Europe, including Bulgaria, industrial and mining activities, coal combustion, and waste disposal have historically contributed to mercury emissions. Many regions in Bulgaria, such as the Maritsa-Iztok basin, the Black Sea coastal area and the Western Rhodopes, have been recognized as areas with potential Hg contamination [6]. Recent investigations demonstrate that even decades after mining and industrial decline, traces of mercury can still be detected in sediments and surface waters.

A detailed review of the presence of mercury in Bulgarian groundwater was recently published by Valtchev et al. [6]. In the study, Hg concentrations were measured in 14 groundwater samples from different hydrogeological zones. Although most samples contained mercury of 0.1 μg L^{-1}, values up to 0.3 μg L^{-1} have been reported in some karst aquifers near industrial areas [6]. These findings suggest local enrichment associated with geological background or anthropogenic influence and confirm that mercury is present even in relatively clean aquifers.

Studies of surface water have provided similar evidence. Mladenova et al. developed an analytical protocol for mercury determination and species analysis in surface waters, allowing the differentiation of mercury species at levels below µg L^{-1}, using solid-phase extraction and cold vapor AAS/ICP-MS [7]. They reported total dissolved mercury concentrations between 0.03 and 0.25 µg L^{-1} in Bulgarian rivers and reservoirs. The authors highlight that some sites near industrial areas show elevated levels compared to background waters, demonstrating the continued importance of national mercury monitoring programs.

In coastal and marine environments, mercury is also a relevant contaminant. Dinkova-Kostova et al. examined heavy metals including mercury in water, sediments and marine fish from Bulgarian Black Sea [8]. Mercury was detected in all three compartments, with sediment concentrations between 0.014 and 0.046 mg kg^{-1} dry weight and fish muscle concentrations up to 0.08 mg kg^{-1} wet weight in *Psetta maxima*. These values are below EU regulatory limits but still indicate a persistently low level of contamination and potential bioaccumulation along the food chain. Comparable observations were made by Peycheva et al. who measured mercury contents in fish from Bulgarian lakes and the Black Sea, obtaining concentrations ranging from 0.02 to 0.16 mg kg^{-1} [9]. Which shows that mercury from water column, sediments and marine habitats bioaccumulates in the food chain

Data on mercury in Bulgarian soils and sediments also confirm the presence of natural and anthropogenic sources. Vitov and Marinova, identified cinnabar (HgS) and other mercury-bearing minerals in stream sediments from ore-bearing zones [10]. This research indicating that natural geological formations may contribute to local mercury enrichment. Meanwhile, Kostova et al. investigated the distribution of mercury in high-sulfur Bulgarian coal and fly ash, revealing that coal combustion remains a significant source of atmospheric and deposited mercury in the region [11, 12].

These findings underline that mercury contamination in Bulgaria, though not extreme, is widespread and environmentally relevant. The reported concentrations are typically below the international guideline value for drinking water (1 µg L^{-1} according to WHO) [13]. However, sediments often show elevated background levels, which can affect the aquatic ecosystem through resuspension or diffusion processes.

Despite the availability of advanced analytical methods, such as cold-vapor atomic absorption spectrometry (CV-AAS), cold-vapor atomic fluorescence (CV-AFS) and inductively coupled plasma mass spectrometry (ICP-MS), the implementation of these techniques is often limited to specialized laboratories. Their high cost, complex maintenance and need for trained personnel restrict routine application, especially in smaller or academic laboratories.

For these reasons, there is renewed interest in simple spectrophotometric approaches that rely on complex formation between mercury ions and organic reagents such as dithizone (diphenyl thiocarbazone). The dithizone method, based on liquid–liquid extraction into chloroform and UV-visible detection, provides a practical and affordable alternative for preliminary assessments and analysing. Although less sensitive than modern techniques, it allows direct visualization of complex formation and can achieve detection limits in the low µg L^{-1} range [13, 14].

The present work focuses on optimizing a UV-Vis spectrophotometric method for determining mercury through complex formation with dithizone and extraction into chloroform. The goal was to define reliable conditions that ensure stable complex formation, good phase separation, and consistent analytical response in aqueous samples. This methodological optimization represents a preparatory stage toward applying the procedure to more complex environmental samples like a sediment or soils after microwave-assisted digestion. In this type of samples problems often arise with matrix effects and interferences are expected to be more significant. Developing a simple, low-cost, and robust analytical procedure like this can strengthen environmental monitoring efforts and provide a useful tool for studying mercury contamination.

EXPERIMENTAL

Instrumentation

Total mercury was measured using Spectroquant® Prove 300 UV/VIS Spectrophotometer 4 nm spectral bandwidth (Merck KGaA, Darmstadt, Germany). Cuvettes with an absorbent layer thickness of 1 cm. For measurements and correction, the pH of the solution was used pH-meter Jenway 3505 with a pH electrode. A centrifuge DLAB DM0506 was used to separate the two liquid phases of different densities, minimizing emulsions and residual microdroplets from the organic phase.

Reagents and solutions

All solutions were prepared using deionized water with a resistivity greater than 18.2 MΩ·cm (Hydrolab R5 system, Warsaw, Poland). 65 % Suprapur Nitric Acid (Merck KGaA, Darmstadt, Germany) was used to acidify the water sample. For pH adjustment, 1 and 2 mol L^{-1} ammonia solution prepared from 25 % ammonia was used and 0.2 mol L^{-1} and 2 mol L^{-1} NaOH solution (Merck KGaA, Darmstadt, Germany). Mercury standard solution for ICP MS (TraceCERT®, 1 g L^{-1} Hg in nitric acid, Merck KGaA, Darmstadt, Germany) was used to prepared standard solution for calibration and spikes. Dithizone (diphenyl thiocarbazone) was used to form a complex with mercury, ACS reagent grade, ≥ 98.0 % (TLC), suitable for UV-Vis spectroscopy, Sigma-Aldrich. To perform the extraction, an organic solvent chloroform was used (suitable for analysis with dithizone, ACS reagent, EMSURE®, Merck KGaA, Darmstadt, Germany).

Sample preparation

A series of standard solutions were prepared with deionized water and acidified with 1 % nitric acid containing a standard mercury solution of 0.80 to 1.10 mg L^{-1} in 15 ml centrifuge tubes. About ~0.50 ml of ammonia solution (1 and 2 mol L^{-1}) was added to reach pH 1.0 ± 0.1. The sample is subjected to successive extraction with a dithizone-chloroform solution (4.00 - 5.00 mg L^{-1}); the total volume of chloroform is 3.00 - 4.00 mL, added in 1.00 mL portions. All prepared samples were shacked for 1.00 min between portion and then centrifuge at 4000 rpm for 20 min. After separation of the organic phase, the absorbance of complex was measured at a wavelength of 488 ± 2 nm. The procedural blank contained all reagents used in the extraction procedure, including nitric acid, ammonia solution, and dithizone-chloroform, but no added mercury. It was processed following the same extraction steps as the samples. All samples were corrected with it. The procedural blank sample shows two characteristic peaks in the spectrum. The first peak is around 440 nm and corresponds to free dithizone, and the second peak is around 605 nm.

RESULTS AND DISCUSSION

Optimization of analytical parameters

The analytical performance of the dithizone-chloroform extraction method was evaluated to establishing reliable operating conditions for UV-Vis determination of mercury. The key experimental factors influencing complex formation and phase transfer were systematically examined. Particular attention was paid to the parameters that affect the equilibrium between the aqueous and organic phases, as they control both the reproducibility and accuracy of the method.

Determination of molar absorptivity of dithizone

The molar absorptivity (Ɛ) of the free dithizone reagent was determined by measuring the absorbance of standard dithizone solutions in chloroform in the concentration range of 7.8×10^{-6} - 3.52×10^{-5} mol L^{-1} at λ_{max} 440 and 605 nm (Fig. 1 and Fig. 2). The molar absorptivity (Ɛ) was determined from the slope of the calibration plot of absorbance (A) versus concentration (C) at λ_{max}, according to the Beer-Lambert law ($A = \varepsilon \cdot b \cdot C$, with b = 1 cm). As the absorbance in the equation is replaced by the value of the slope from the equation of the corresponding calibration line. The obtained values, $\varepsilon_{440} = 7.10 \times 10^3$ L mol^{-1} cm^{-1} and $\varepsilon_{605} = 1.68 \times 10^4$ L mol^{-1} cm^{-1}, are consistent with reported data for dithizone in chloroform. Christensen and Madsen, reported Ɛ values of approximately 1.6×10^4 L mol^{-1} cm^{-1} at 605 nm and 7×10^3 L mol^{-1} cm^{-1} at 440 nm, confirming the reliability of the present measurements [15]. Slight deviations at higher concentrations may be attributed to dimerization or solvent effects.

In parallel, the absorbance of the sample was measured after the formation of a complex between dithizone and Hg^{2+} at a maximum of $\lambda_{max} = 488$ nm, Ɛ increased to $\approx 6.6 \times 10^4$ L mol^{-1} cm^{-1}, which indicates a significant increase in the absorbance. This indicates that the sensitivity of the method is increased for the quantitative determination of mercury.

Stoichiometry of the complex (mole-ratio method)

The stoichiometric ratio between mercury and dithizone was investigated using the mole-ratio method at constant mercury concentration and varying dithizone levels. In the mole-ratio experiment, the absorbance of the Hg^{2+}- dithizone complex reached a plateau at approximately 3 - 4 mol eq. of dithizone per mole of Hg (Fig. 3). Under the conditions of the routine extraction (5.00 mL aqueous sample containing 1.00 mg L^{-1} Hg and 3.00 mL chloroform containing 5.00 mg L^{-1}

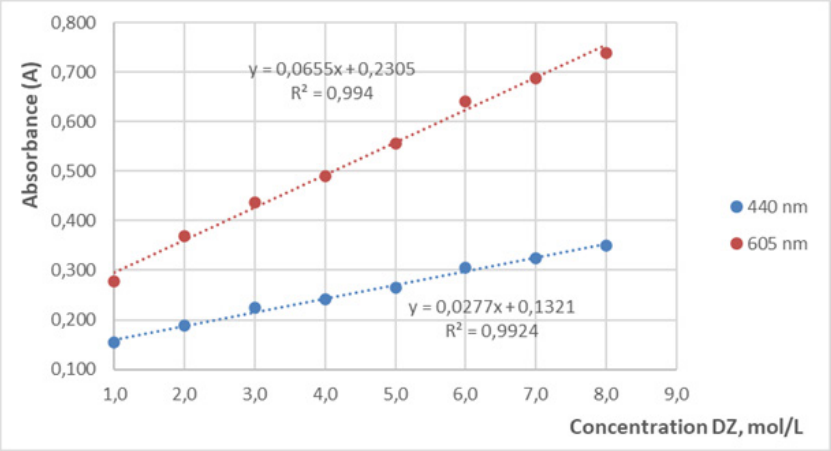

Fig. 1. Calibration lines at λ_{max} = 440 and λ_{max} = 605 nm for calculating molar absorbance.

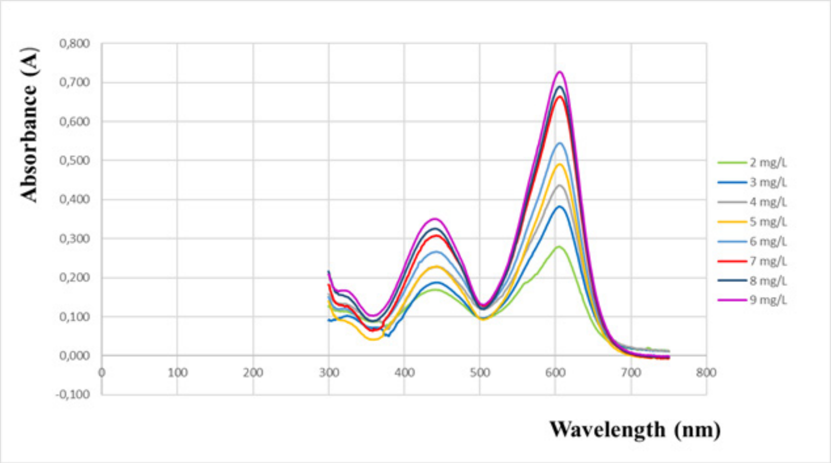

Fig. 2. Spectra of dithizone in chloroform by measuring the absorbance of standard solutions in the concentration range of 1.00 - 9.00 mg L^{-1} at λ_{max} = 440 and λ_{max} = 605 nm.

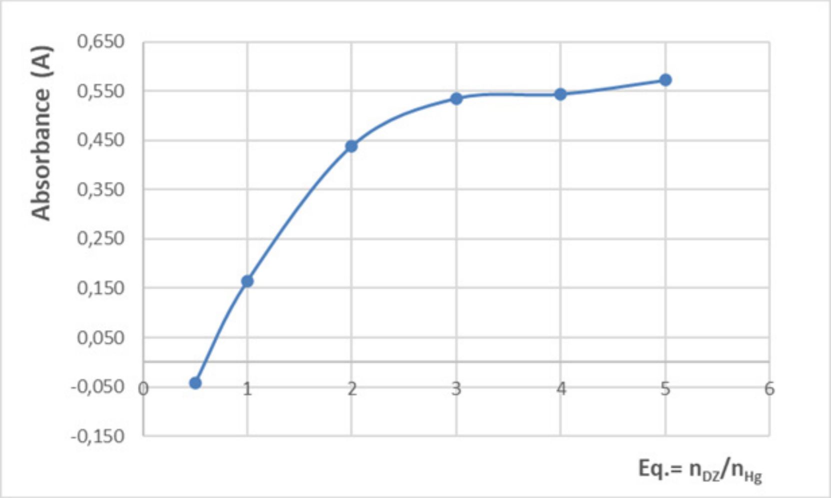

Fig. 3. Graph of Hg^{2+}- dithizone mole-ratios vs. absorbance.

dithizone), the calculated molar ratio $n_{Dz}/n_{Hg} \approx 2.35$, i.e., slightly below the plateau region. Calculation details: 5.00 mL of 1.00 mg L^{-1} Hg contains 2.49×10^{-8} mol Hg, while 3.00 mL of 5.00 mg L^{-1} dithizone provides 5.85×10^{-8} mol dithizone, giving a ratio Dz : Hg ≈ 2.35. To reach the experimentally observed plateau (3 - 4 eq.), the dithizone concentration in 3.00 mL would need to be increased to approximately 6.40 - 8.50 mg L^{-1}. Alternatively, maintaining the total dithizone mass while increasing the organic phase volume to 4.00 mL would lower the required concentration to around 4.80 mg L^{-1} for a 3:1 ratio.

In this study, 5.00 mg L^{-1} dithizone in 4.00 mL chloroform was chosen as a practical compromise between reagent excess and analytical sensitivity. This concentration ensures effective complexation of mercury over the entire calibration range and avoids oversaturation in low-concentration standards. This compromise option also, ensure sufficient reagent availability for higher mercury levels. Such a balance was essential to achieve consistent extraction efficiency and reproducible absorbance without excessive reagent background.

Absorbance - concentration relationship of dithizone

The applicability of the Beer-Lambert law was verified under the experimental conditions by examining the linear relationship between absorbance and dithizone concentration in chloroform in the range 0.80 to 10.00 mg L^{-1}. The Hg-dithizone complex was not used for this test because its absorbance depends on several factors, including complex stoichiometry, pH, and extraction efficiency. The study of dithizone in chloroform is a control experiment that proves that the dithizone-chloroform-spectrophotometer system is photometrically linear in the selected range, and that any deviations obtained during the analysis of the complex are due to chemical processes, and not to instrumental or optical limitations. The obtained linear range defines the optimal concentration range for subsequent photometric determination of mercury.

The absorbance - concentration relationship of dithizone in chloroform was linear (Fig. 4) between 4.00 to 8.00 mg L^{-1}, with a correlation coefficient ($R^2 = 0.9933$ for λ_{440} and 0.9916 for λ_{605}). At higher concentrations, a slight deviation from linearity was observed, likely due to self-absorption or molecular aggregation of dithizone [16]. Absorbance at 605 nm was more intense and more sensitive to concentration changes, whereas the 440 nm signal was weaker but more stable. For quantitative measurements, a range where both wavelengths showed linear behaviour was selected.

Effect of pH on complex formation

The effect of pH on the absorbance of the Hg^{2+}-dithizone complex was studied using solutions containing 1.00 mg L^{-1} Hg^{2+} and a fixed dithizone concentration of 4.00 mg L^{-1} in chloroform. The pH of the aqueous phase was adjusted with ammonia solution in the range 0.5 - 5.0. Ammonia can react with Hg^{2+} to

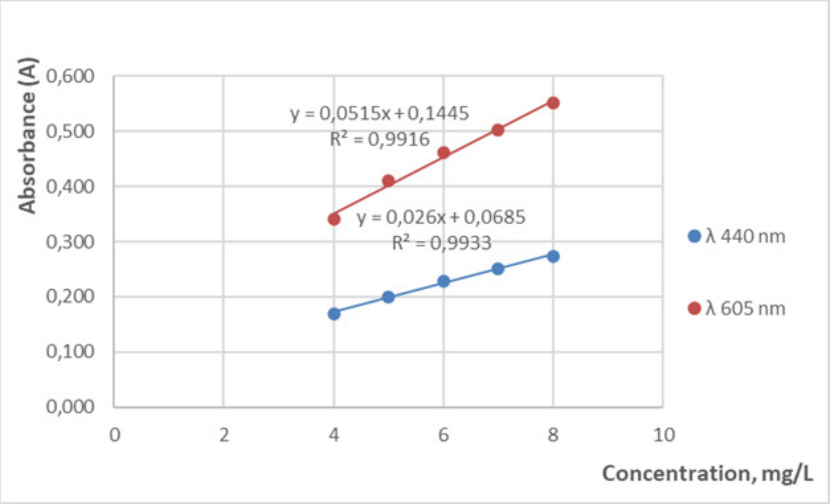

Fig. 4. Absorbance of dithizone in chloroform at $\lambda_{max} = 440$ and $\lambda_{max} = 605$ nm as a function of concentration. A linear response is maintained up to approximately 4.00 - 8.00 mg L^{-1}.

form insoluble basic mercuric amido compounds [16, 20]. In our system, controlled addition of ammonia likely minimizes precipitate formation, thereby helping to maintain a sufficient concentration of free mercury (Hg^{2+}) for complex formation.

The dependence of absorbance on pH (Fig. 5) clearly shows that the Hg^{2+}-dithizone complex shows maximum stability in the acidic to mildly acidic range (pH ≈ 1.0 - 1.5), where absorbance reached ~ 0.600 - 0.610. As pH increases beyond ~2.0, a pronounced decrease in absorbance is observed, reaching a minimum around pH 3.5 - 4.0 (~ 0.530). Beyond this point, a slight recovery in absorbance occurs at pH ~5.0 (to ~ 0.545). Fig. 6 shows the spectra of the Hg^{2+}- dithizone complex at different pH.

These results indicate that at lower pH complex formation is favourable, while at higher pH the equilibrium shifts, probably due to competitive hydrolysis of Hg^{2+} or protonation/deprotonation of the ligand, which reduces the stability of the complex. The slight increase at pH 5.0 may indicate partial stabilization under mildly alkaline conditions, but still significantly below the acidic optimum.

Ahmed and Alam, report that Hg^{2+}-dithizone complex formation proceeds optimally in mildly acidic conditions, and higher basicity disrupts colour intensity [17]. Ely described that extreme alkalinity destabilizes the complex [18]. Braun and Farag also emphasizes the sensitivity of Hg^{2+}-dithizone interactions to pH and chelating agent concentrations [19].

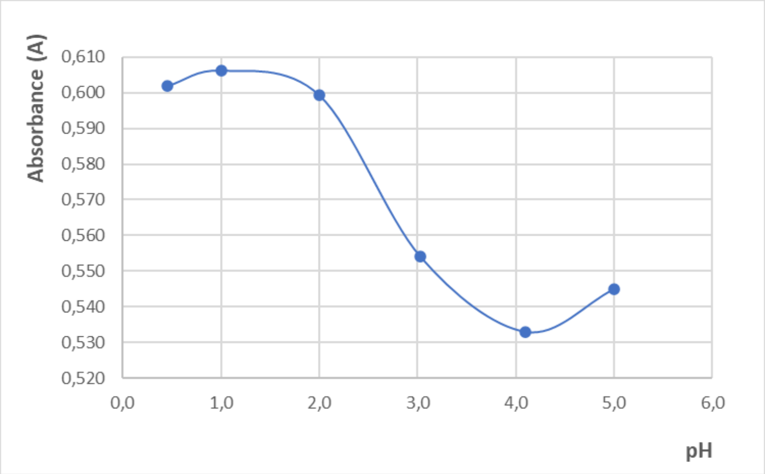

Fig. 5. Dependence of the absorbance on pH of Hg^{2+}-dithizone complex.

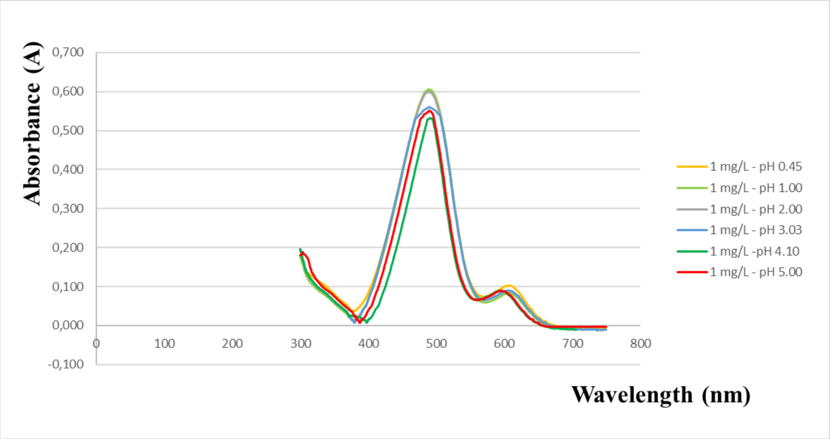

Fig. 6. Spectra of Hg^{2+}-dithizone complex at different pH.

In our method, ammonia was used as a milder pH-adjusting reagent, presumably avoiding the abrupt pH changes caused by NaOH. The use of ammonia allows better control of the water balance and helps minimize hydrolysis and precipitation of mercury. In contrast, direct addition of NaOH can lead to locally high OH^- concentrations, promoting the formation of poorly soluble $Hg(OH)_2$ and reducing the availability of free Hg^{2+} ions [20].

Based on these observations, for further analyses (calibration, extraction) the optimal pH window is set around 1.0 - 1.5 ± 0.1, ensuring maximal complex formation and stability.

Optimization of aqueous phase volume

To evaluate the efficiency of mercury ion extraction with dithizone in chloroform, the effect of the aqueous sample volume was studied while keeping the volume and concentration of the organic phase constant. The aim of this experiment was to determine the aqueous phase volume that allows maximum transfer of Hg^{2+} to the organic phase and the highest analytical sensitivity. Additionally, by analysing the linear relationship between absorbance and sample volume ($1/A$ vs. $1/V_{aq}$), the distribution constant (D) of the complex between the aqueous and organic phases could be estimated, and the fraction of extracted Hg^{2+} (*f*) could be calculated.

Samples with a mercury concentration of 1.00 mg L^{-1} and aqueous phase volumes of 3.00, 5.00, 7.00, and 10.00 mL were used. To each sample, 4.00 mL of dithizone in chloroform (5.00 mg L^{-1}) was added. After extraction, the organic phase was separated and measured three times spectrophotometrically at λ_{max} = 488 nm.

The results showed that absorbance increased with increasing aqueous volume, reaching a slight plateau between 5.00 and 7.00 mL. This behaviour can be explained by the change in the phase volume ratio (V_{aq}/V_{org}) and the distribution of the complex between the two phases. The distribution constant (D) for the Hg^{2+}-dithizone complex between water and chloroform was experimentally determined to be approximately 11. This value indicates efficient transfer of mercury to the organic phase, as $D >> 1$ in a single extraction step [21]. The obtained D value agrees well with literature data for Hg^{2+}-dithizone systems, confirming the validity of the applied conditions and demonstrating that the extraction equilibrium was effectively reached [22, 23].

Fig. 7 shows the relationship between the aqueous sample volume (V_{aq}) and the extraction efficiency of Hg^{2+}. The results indicate a clear decrease in extraction efficiency with increasing aqueous volume from 91.9 % at 3.50 mL to 79.4 % at 10.30 mL. This effect is due to the change in the V_{aq}/V_{org} ratio, where larger aqueous volumes reduce the amount of Hg^{2+} distributed per unit volume of organic phase. At small sample volumes (3.00 - 5.00 mL), extraction is almost complete, indicating an excess of dithizone and a shift of the equilibrium towards the formation of the Hg^{2+}-dithizone complex in the organic phase. As V_{aq} increases above

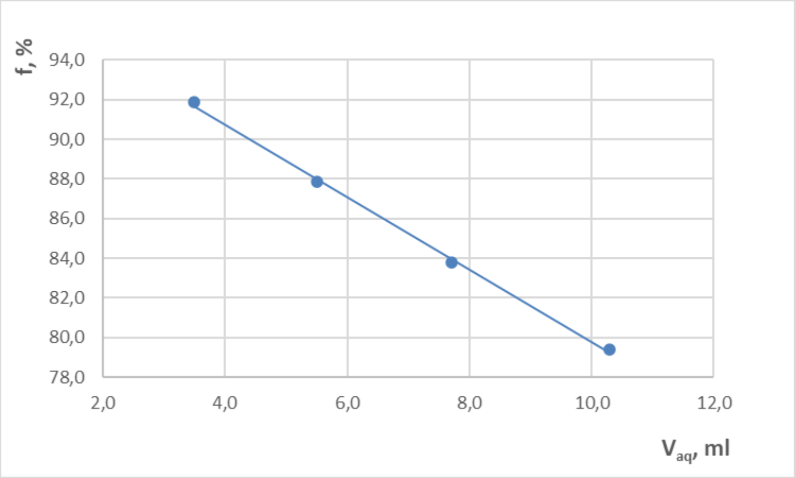

Fig. 7. Relationship between water sample volume (V_{aq}) and extraction rate (%f).

7.00 mL, part of the metal remains in the aqueous phase, reducing extraction efficiency and lowering f (%).

These results confirm that the optimal phase ratio is approximately 1:1 (V_{aq}/V_{org}), which ensures high extraction efficiency (> 85 %) with stable spectrophotometric signals [21].

Effect of shaking time and extraction efficiency

The influence of shaking time on the absorbance of the Hg^{2+}-dithizone complex was assessed using solutions with 1.00 mg L^{-1} Hg^{2+} and corrected dithizone concentration, with pH 1.0 ± 0.1 with NH_3 solution. The absorbance as a function of shaking time (Fig. 8) shows a clear maximum at ~ 60 s (~0.347), followed by a decline to ~0.305 at ~180 - 200 s. A moderate rebound to an absorbance of ~0.324 at ~240 - 260 s.

These results indicate that equilibrium between the aqueous and organic phases is achieved rapidly (within ~ 60 s). After which prolonged shaking may lead to microemulsion formation, back-diffusion, or increased dispersion of fine droplets, reducing absorption. The slight recovery at longer times may reflect re-equilibration or improved phase contact after droplet sedimentation.

Skoog et al. discussed similar behaviour that excessive agitation can degrade extraction efficiency, possibly by introducing emulsions or destabilizing phase boundaries. In other spectrophotometric extraction systems, a plateau or decline after optimal mixing time is common [24].

Based on these observations, the optimal shaking time for highest extraction efficiency is set at ~ 60 s. The longer times do not increase and may even decrease absorbance, so this duration is recommended for calibration and sample processing.

Calibration curve and application to spiked tap and deionized water samples

A calibration curve (Fig. 9) was constructed using standard mercury solutions in the range 0.80 - 1.10 mg L^{-1}, extracted under optimized conditions (pH 1.0 ± 0.1 corrected with HN_3, stepwise addition of the organic phase of 4 × 1.00 mL, 5.00 mg L^{-1} dithizone-chloroform, 1.00 min shaking and after that centrifugation for 20 min at 4000 rpm). The samples were measured in triplicate, taking the average absorbance at λ_{max} = 488 ± 2 nm and correcting the results with the absorbance obtained from a triplicate procedural blank

A concentration of 0.85 mg L^{-1} of mercury standard solution was added to the tap water sample and 1.00 mg L^{-1} of mercury standard solution was added to the deionized water sample. The linear regression Eq. (1) was:

$$A = 0.2926C + 0.0029 \quad (1)$$

where A is the absorbance and C is mercury concentration (mg L^{-1}), with $R^2 = 0.9981$.

The analytical recovery was between 71 % for the deionized water sample and 74 % for the tap water sample. The analytical recovery obtained for the deionized and tap water samples (71 - 74 %) showed

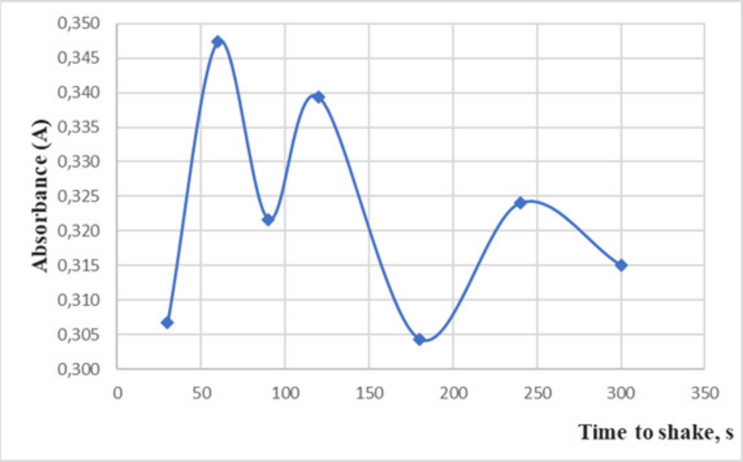

Fig. 8. Absorbance as a function of extraction time.

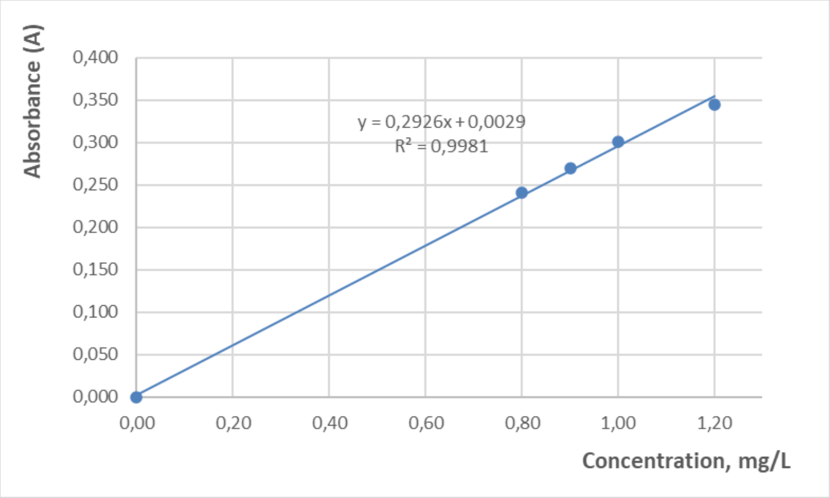

Fig. 9. The calibration curve using the external standard method for the quantitative determination of spiked mercury in tap water.

satisfactory extraction efficiency under the optimized conditions. Although slightly below the theoretical value (~ 85 %) predicted by the partition model. The difference could be due to partial transformation of the mercury species during pH adjustment with ammonia, leading to the formation of mercury-ammonia complexes (Hg-NH_3) that are less accessible for extraction with dithizone. Incomplete equilibration between the two phases during the shaking step could also contribute to small losses, as could adsorption of mercury on the vessel walls. According to the European Commission and US EPA guidelines for the validation of analytical methods, acceptable analytical recovery from extraction should generally be in the range of 80 to 120 % [25, 26]. Although the recoveries obtained in the present study are slightly below these recommended values, they are still within practical acceptable limits.

Although spectrophotometric methods are less sensitive than CV-AAS or ICP-MS, they remain valuable for preliminary monitoring and educational applications. The obtained optimized parameters for complexation of mercury with dithizone and its extraction into the organic phase are comparable to results obtained by other authors [13, 14, 17]. Overall, the optimization results demonstrate that the dithizone-based spectrophotometric method provides a reliable and low-cost alternative for mercury determination in water and sediments, with acceptable linearity and recovery.

CONCLUSIONS

The present study demonstrates that a simple UV-Vis spectrophotometric method based on dithizone extraction can be optimized to achieve results close to regulatory requirements for mercury determinations in aqueous matrices. By controlling the stoichiometry of the reagents, phase ratios, and extraction parameters, analytical precision comparable to that of state-of-the-art techniques was achieved at significantly lower costs. The optimized procedure establishes a methodological basis for extending the approach to complex matrices, such as digested sediments or soils, contributing to accessible and sustainable mercury monitoring in environmental laboratories.

Acknowledgments

This research is supported by the Bulgarian Ministry of Education and Science under the National Program “Young Scientists and Postdoctoral Students -2”.

Authors’ contributions

V.I.: developed the concept and methodology of the study; V.I. and K.M. carried out the experiments and performed the statistical analysis; V.I.: wrote the original version of the manuscript; K.Ch. performed the revision and contributed to the editing of the manuscript.

REFERENCES

1. S. Covelli, J. Faganeli, M. Horvat, A. Brambati, Mercury contamination of coastal sediments as the result of long-term cinnabar mining activity (Gulf of Trieste, northern Adriatic Sea), Appl. Geochem., 16, 2001, 541-558.
2. W.F. Fitzgerald, C.H. Lamborg, C.R. Hammerschmidt, Chem. Rev., 107, 2, 2007, 641-662.
3. U. Kwasigroch, K. Łukawska-Matuszewska, A. Jędruch, O. Brocławik, M. Bełdowska, Mar. Environ. Res., 191, 2023, 106132.
4. D. O'Connor, D. Hou, Y.S. Ok, J. Mulder, L. Duan, Q. Wu, S. Wang, F.M.G. Tack, J. Rinklebe, Mercury speciation, transformation, and transportation in soils, atmospheric flux, and implications for risk management: A critical review, Environ. Int., 126, 2019, 747-761.
5. UNEP, Global Mercury Assessment 2018, United Nations Environment Programme, Chemicals and Health Branch, Geneva, 2019.
6. S. Valtchev, L. Bidzhova, A. Toteva, S.V. Georgiev, S. Kolev, Overview of mercury occurrence in Bulgarian groundwater: Preliminary data, Rev. Bulg. Geol. Soc., 85, 3, 2024, 249-252.
7. E. Mladenova, I. Dakova, D. Tsalev, I. Karadjova, Mercury determination and speciation analysis in surface waters, Open Chem., 10, 4, 2012, 1175-1182.
8. M. Dinkova-Kostova, M. Stancheva, K. Peycheva, Heavy metals in water, sediments and marine fishes from the Bulgarian Black Sea, in: Proceedings of EMECS-10, Monaco, 2017.
9. K. Peycheva, L. Makedonski, S. Georgieva, M. Stancheva, Assessment of mercury content in fish tissues from Bulgarian lakes and the Black Sea, Ecol. Safety, 9, 1, 2015, 43-48.
10. O. Vitov, I. Marinova, Natural potential sources for mercury pollution in Bulgaria, J. Min. Metall., 50, 2, 2014, 123-132.
11. I.J. Kostova, J.C. Hower, M. Mastalerz, S.V. Vassilev, Mercury capture by selected Bulgarian fly ashes: Influence of coal rank and fly ash carbon pore structure on capture efficiency, Appl. Geochem., 26, 1, 2011, 18-27.
12. FAO/WHO, Measurement Uncertainty - CXG 54-2004, 2023.
13. J. Zhang, W. Zhang, Y. Jin, Sensitive determination of trace mercury by UV-visible diffuse reflectance spectroscopy after complexation and membrane filtration-enrichment, Spectrochim. Acta A, 87, 2012, 265-270.
14. A. Afkhami, T. Madrakian, S.J. Sabounchei, Cloud point extraction and spectrophotometric determination of trace mercury(II) using dithizone, J. Hazard. Mater., 174, 1-3, 2010, 451-456.
15. R.W. Christensen, R.M. Madsen, Determination of mercury(II) concentration in water using dithizone, Bachelor's Thesis, Aarhus University, Department of Chemistry, Denmark, 2019.
16. G. Svehla, Vogel's Qualitative Inorganic Analysis, 7th ed., Longman, 1996
17. M.J. Ahmed, M.S. Alam, A rapid spectrophotometric method for the determination of mercury in environmental, biological, soil and plant samples using diphenylthiocarbazone, Spectroscopy, 17, 2003, 45-52.
18. C.T. Elly, Dithizone procedure for mercury analysis, J. Water Pollut. Control Fed., 45, 5, 1973, 940-945.
19. T. Braun, A.B. Farag, Plasticized open-cell polyurethane foam as a universal matrix for organic reagents in trace element preconcentration: Part II. Collection of mercury traces on dithizone and diethyldithiocarbamate foams, Anal. Chim. Acta, 71, 1, 1974, 133-140.
20. W. Stumm, J.J. Morgan, Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters, 3rd ed., John Wiley & Sons, New York, 1996.
21. G.D. Christian, Analytical Chemistry, 6th ed., Wiley, New York, 2004.
22. Z. Marczenko, Separation and Spectrophotometric Determination of Elements, Ellis Horwood, 1986, 48-52.
23. E.B. Sandell, Colorimetric Determination of Traces of Metals, 3rd ed., Interscience, New York, 1959.
24. D.A. Skoog, F.J. Holler, S.R. Crouch, Principles of Instrumental Analysis, 7th ed., Brooks Cole, Boston, 2017.
25. European Commission, Technical Guideline on the Evaluation of Extraction Efficiency of Residue Analytical Methods, SANTE/2017/10632, Rev. 5, 11 May 2023
26. EPA Method 3500C, Organic extraction and sample preparation, Revision 3, February 2007.