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A novel optical chemical sensor for germanium determination in food and environmental samples

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A colorimetric optode for germanium (Ge^{4+}) detection was developed by incorporating 2-(((3,5-dimercapto-4*H*-1,2,4-triazole-4-yl)imino)methyl) phenol (DMTMP) and the liquid ion-exchanger trioctylmethylammonium chloride (Aliquat-336) into a cellulose triacetate (CTA) matrix plasticized with tri-(2-ethylhexyl) phosphate (TEHP). The transparent optode quantitatively preconcentrates Ge^{4+} from aqueous samples, inducing a distinct color change ($\lambda_{max} = 545$ nm). Optimal equilibration was achieved in 5.00 min in borate medium and 25.0 min in natural water. On the other hand, an optode sample without Aliquat-336 showed no change in color corresponding to the Ge^{4+}-DMTMP complex after equilibration with the same aqueous solution containing the Ge^{4+} ions. The uptake of Ge^{4+} is pH dependent and at pH 7.50 the maximum uptake was greater than 97.5 percent. In the detection of the Ge^{4+} ion, no significant interference of more than 750 times the concentration of the number of potentially interfering ions was detected. This optode showed a linear increase in absorbance at 545 nm with a peak absorbance of 545 nm for a concentration range of 6.00 to 174 ng mL^{-1} of G^{4+} ions in aqueous solution over 5.00 min. The detection and quantification limits were assessed as 1.75 and 5.75 ng mL^{-1}, respectively. The optode proposed in this study has been proven to be reusable. The optode is an effective tool for the detection of germanium in food and environmental samples with high accuracy and selectivity.

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Introduction

Winkler first identified germanium in 1885,[1] and since then, many studies have explored its properties and compounds. Although germanium may be essential to evolution, it can also adversely affect basic biological functions. Research focused on the effects of germanium compounds on living organisms and on human health, including their ingestion and associated health risks.[2–5] It is a key ingredient in a wide range of technological applications, including spiro-germanium for cancer therapy, high refractive-index glass, corrosion inhibitors in alloys, phosphors, identification systems, and infrared sensing devices. Global production of germanium-based products is growing, which is leading to a gradual increase in environmental germanium concentration.[6,7]

Germanium is naturally rare, with an average concentration of only 1.50 μg mL^{-1} in the Earth's crust.[8] Germanium is a grey-white semiconductor element with properties similar to those of metals and insulators, along with physicochemical characteristics similar to silicon and tin. Due to its different physicochemical properties and compounds, it has found applications in a wide range of industrial and advanced technological sectors.[9–11] The assessment of trace and ultra-trace concentrations of germanium in environmental matrices has become of considerable importance.[12]

Germanium is considered to be a scarce and strategically important element,[13] and its unique properties are increasingly utilized in renewable energy technologies and in electronic devices. The increasing use of graphene in emerging technologies, including semiconductor sensors, optical systems, wind energy, solar cells and electronic devices, has raised concerns about its potential environmental impact, in particular landfills.[14,15] Growing industrial interest in this element necessitates an evaluation of its potential environmental effects.[16] Classified as one of the Technology Critical Elements (TCE),[17–19] germanium plays a significant role in various technological and industrial applications, including semiconductor sensors, optical systems, telecommunications, wind energy systems, electric vehicles, solar cells, and energy-saving lighting solutions.[20] The growing reliance on advanced technologies results in the continuous discharge of increasing amounts of TCE into the environment. As a result, the scientific community has increased its interest in the natural processes associated with TCEs, their effects on living organisms, and their potential risks for human health.[21] Therefore, it is crucial to track the presence of this element in food, soil, water, and other possible intake sources, as well as to measure its levels in biological

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tissues using accurate and highly selective analytical techniques.

The detection of trace amounts of germanium in food has attracted interest because of its important role in promoting hygienic food quality and its potential anti-cancer properties.[22] Intake of germanium dioxide is associated with serious adverse effects, such as organ failure and possibly fatal outcomes. Globally, the average concentration of germanium (Ge) in surface soils is approximately 2.00 mg kg^{-1}, with ranges ranging from 0.10 mg kg^{-1} to as high as 15.00 mg kg^{-1}, due to different soil types formed under different geological and environmental conditions.[23] The concentration of germanium in soils worldwide is influenced by both natural (geogenic) and human-related (anthropogenic) factors. For instance, research carried out in the mining area of Freiberg, Germany, has shown a large variation in the total Ge levels in soil, with values ranging between 1.00 and 4.30 mg kg^{-1} and a mean concentration of 1.90 mg kg^{-1}.[24]

Currently, the most widely used analytical methods for determining germanium are spectrometric techniques, such as atomic absorption spectroscopy (AAS),[25] inductively coupled plasma mass spectrometry ICP-MS,[26,27] inductively coupled plasma optical emission spectroscopy ICP-OES,[28] high resolution inductively coupled plasma mass spectrometry HRICP-MS,[29] laser ablation inductively coupled plasma mass spectrometry LA-ICP-MS,[30] and spectrophotometry.[31–34] The applicability of certain methods, especially in fieldwork and laboratories within developing nations, may be constrained by factors such as the instrument's initial cost, required technical expertise, expenses for consumables, and equipment maintenance. The spectrophotometric method is preferred in this instance because of its user-friendliness and relatively low costs. In recent years, various newly developed compounds known as optical chemosensors have been studied as analytical agents for the spectrophotometric detection of germanium(IV) ions,[35,36] and other metal ions.[37–39]

Optical chemical sensors (or optodes) provide a simple and cost-efficient method for measuring the concentrations of different cations, anions, and some molecular substances.[40,41] In the last 30 years, optical chemical sensors have been developed with considerable interest.[42–44] Many of them are based on spectrophotometric measurements; however, no optode have been developed for detection of cations of specific elements. Most optodes use reagents to form complexes with metal ions. Various techniques are used to immobilize ion indicators on/in membranes, including covalent bonding to a functionalized support,[45,46] or physical entrapping in a porous polymer matrix or behind a selectively permeable membrane.[47,48] Preferably, the immobilized ionic reagent must remain retained and not leach into the sample solution throughout the analyte measurement process.

This study presents the development of a Ge^{4+} optode by immobilization of DMTMP reagent and Aliquat-336 in a CTA membrane that has been plasticized with TEHP. In this study, DMTMP incorporated into the matrix of optode itself did not show any interaction with Ge^{4+} ions. However, the presence of Aliquat-336 increases the transport of Ge^{4+} in the optode. The key parameters influencing the design and performance of the sensor shall be systematically assessed and optimized. The influence of different experimental factors—including pH levels, borate ion concentration, and the existence of interfering cations and anions—on the identification of Ge^{4+} was examined, along with its preconcentration from large volumes of water and the potential for optode reuse. The optimized optode formulation and adjusted chemical parameters of the aqueous media were used for the quantification of both the Ge^{4+} and CH_3Ge^{4+} species. Subsequently, the Ge^{4+}-loaded optodes were used to enhance the colorimetric analysis of Ge^{4+} in a variety of food and environmental water samples.

Experimental

Apparatus

A Fisons (UK) double distiller, made entirely of glass, was employed to prepare deionized water. A Jenway 3505 pH meter (9V AC-powered) was utilized to detect pH values. A digital micrometer (Mitutoyo, Japan) featuring an accuracy of ±0.001 mm was employed to detect the thickness of the membrane samples. Optode samples were placed within a quartz cuvette (dimensions: 3 cm × 1 cm × 1 cm), and their absorbance spectra were measured with a UV-Visible spectrophotometer (model V-530, JASCO, Tokyo, Japan). For each set of samples, blank measurements were conducted. Ge(IV) ion quantification was performed using ICP-AES (PerkinElmer, Germany, 8300).

Materials

Analytical-grade chemicals including dichloromethane, copper chloride, zinc acetate, lead nitrate, ferrous sulfate, cadmium nitrate, and mercuric chloride were procured from Merck (Mumbai, India; Germany, 8300). Throughout the current studies, deionized water (18 MΩ cm^{-1}) was utilized. Aliquat-336 from Sigma-Aldrich (Steinheim, Switzerland) and Cellulose triacetate (molecular weight 72 000–74 000, acetyl value = 43.2%) (CTA), and tri-(2-ethylhexyl) phosphate (TEHP) sourced from Koch-Light Laboratories (Coinbrook Bucks, England) and GeO_2 (spectrometrically pure that was obtained from the Shanghai Third Chemical Factory, Shanghai, China) were used as obtained. Dioctylphthalate (DOP) and *o*-nitrophenyloctyl ether (NPOE) were obtained from Fluka (situated in Busch, Switzerland) and used without additional purification.

A 100.0 μg mL^{-1} germanium(IV) stock solution was prepared by gently heating 0.0144 g of high purity GeO_2 in 20.0 mL of 2.00% sodium hydroxide solution until completely dissolved. Hydrochloric acid was added until the solution was colorless, then the solution was transferred to a 100.0 mL standard flask and brought to the volume with water. Standard working solutions of 1.00 μg mL^{-1} were obtained by appropriate dilution with water. Fresh dilution preparations were prepared as necessary.

For the assessment of the potential impact of interfering ions, stock solutions (mg L^{-1}) of various metal ions were prepared from high-purity nitrate or chloride salts (≥99.99%).

All experiments were conducted using deionized water. A pre-prepared borate buffer, maintaining a pH between 5.65 and 10.50, was used to stabilize the pH of the solutions.[49]

Synthesis of (DMTMP) schiff base

Initially, 4-amino-3,5-dimercapto-1,2,4-triazole was prepared as described by the published method.[50] Next, two drops of piperidine were introduced to a suspension of 4-amino-3,5-dimercapto-1,2,4-triazole (1.48 g, 10.0 mmol) in absolute ethanol and an equimolar amount of salicyaldhyde (10.0 mmol) in ethanol (10.0 mL). The reflux of the reaction mixture was achieved in 5.00 h by means of a water bath and continuous stirring. After washing the precipitate with warm ethanol, it was filtered, dried on a water bath, recrystallized using bi-distilled water, and finally dried in the air. The product had a melting point of 287–288 °C. Anal. Cal. For $C_9H_8N_4OS_2$ (M.wt = 252.31): C, 42.84; H, 3.20; N, 22.21; O, 6.34; S, 25.41%. Found: C, 42.91; H, 3.23, N, 22.24.; O, 6.45; S, 25.40%. The molecular structure of the Schiff base compound has been confirmed by FT-IR spectroscopy and (^{1}H-NMR) techniques (Fig. 1). The synthetic route used for the preparation of the Schiff base reagent 2-(((3,5-dimercapto-4*H*-1,2,4-triazole-4-yl)imino)methyl)phenol (DMTMP) is shown in Scheme 1.

Preparation of optode

CTA (0.10 g) was dissolved in 10 mL dichloromethane. The solution was prepared by the dissolution of TEHP (0.10 g), Aliquat-336 (0.04 g), and DMTMP (0.01 g) in 5.00 mL dichloromethane. The two solutions were combined and ultrasonicated for 2.00 minutes to produce a uniform casting

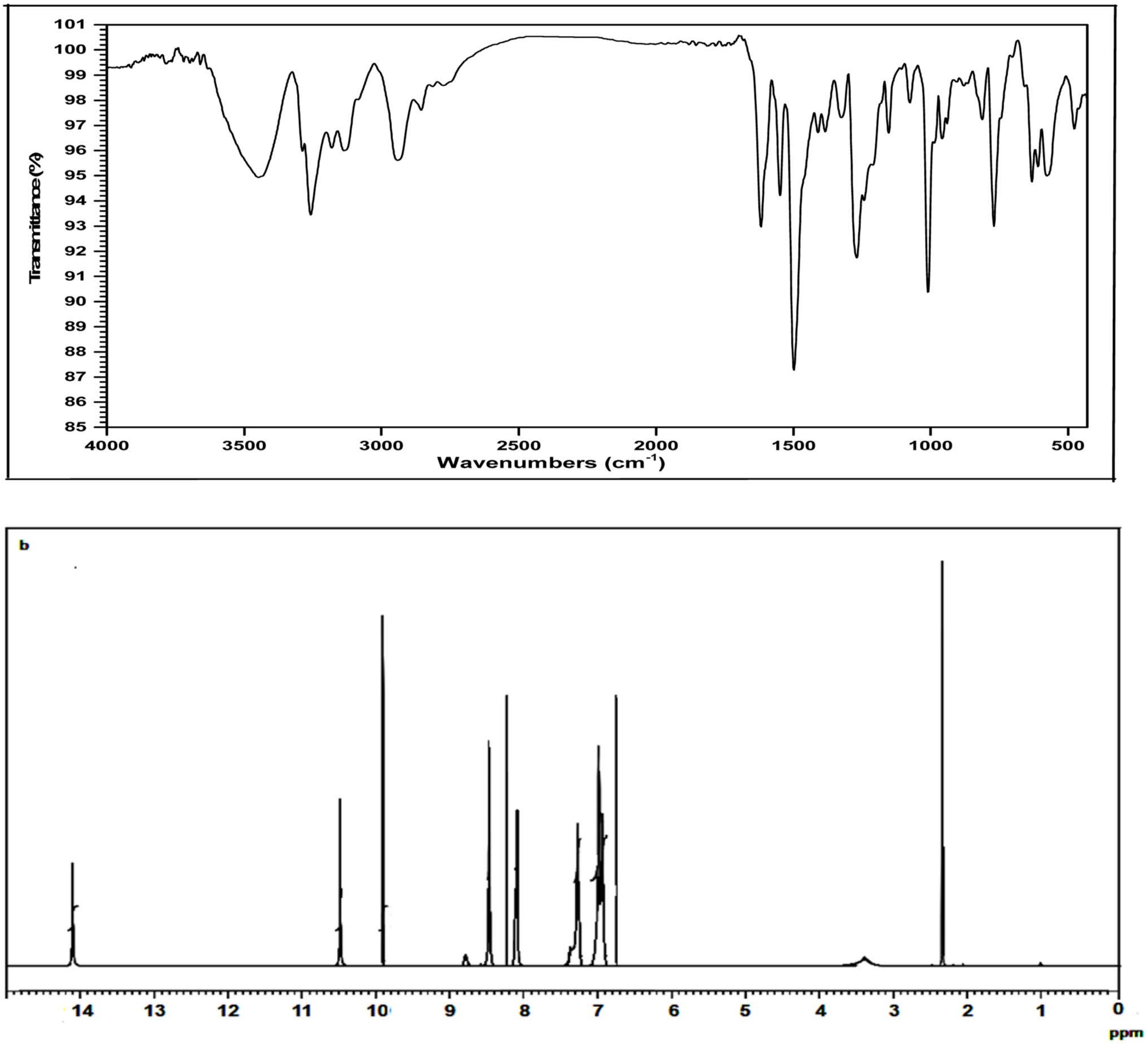
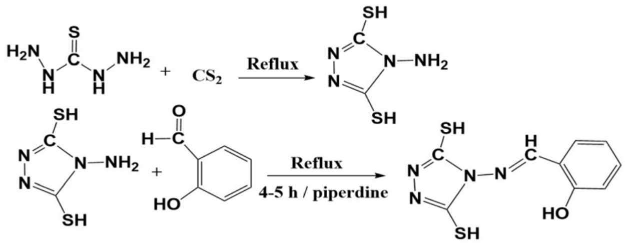


Fig. 1 (a) FT-IR and (b) ^{1}H-NMR spectra of DMTMP.



Scheme 1 Synthetic pathway for the preparation of DMTMP Schiff base reagent.

solution. The casting solution was poured into a Petri dish (9 cm inner diameter) placed on a flat, level surface. The lid was partially closed to enable gradual evaporation of CH_2Cl_2 from the solution. After two days of evaporation of dichloromethane from the casting solution, the transparent optode was carefully removed the Petri dish. The resulting optode was self-supporting and showed sufficient mechanical strength for use in stirred aqueous solutions. Consequently, transparent support was not necessary. The prepared optode was then washed thoroughly with water to eliminate any soluble residues which have been present. The measurements showed that the optode membrane is 38 ± 5.00 μm thick. Optode samples remained at a fixed size of 2 cm × 1 cm during the investigation.

General procedure

The formation of the Ge^{4+}–DMTMP complex in the optode sample was spectrophotometrically monitored, with its intensity measured relative to the Ge^{4+} concentration in the equilibration solution. The pH of the equilibration solutions (2.50 mL) was maintained at 7.50. The known amount of Ge^{4+} (6.00–174 ng mL) was added to the equilibration solution, together with 2.50 mL of borate buffer solution (pH 7.50). Measurements of absorbance for the Ge^{4+}-loaded optode samples were taken at $\lambda_{max} = 545$ nm. To investigate the kinetics, the optode was immersed in a thoroughly stirred solution containing a defined concentration of Ge^{4+} in a borate buffer at pH 7.50. After equilibration for a specified time, the optode was removed from the solution, and its absorbance was recorded at 545 nm. The equilibration of the optode sample was allowed to proceed until a stable absorbance reading was obtained. To study the desorption of Ge^{4+}, the optode sample was immersed in 10.0 mL of 0.15 M HCl aqueous solution for a specific time with constant stirring. The release of Ge^{4+} from the optode was tracked by measuring the absorbance of the optode sample at 545 nm. Scheme 2 shows a schematic representation of the immobilization process of DMTMP on the membrane and the resulting change in color of the thin film after and prior to exposure to the Ge^{4+} solution.

Determination of stoichiometry

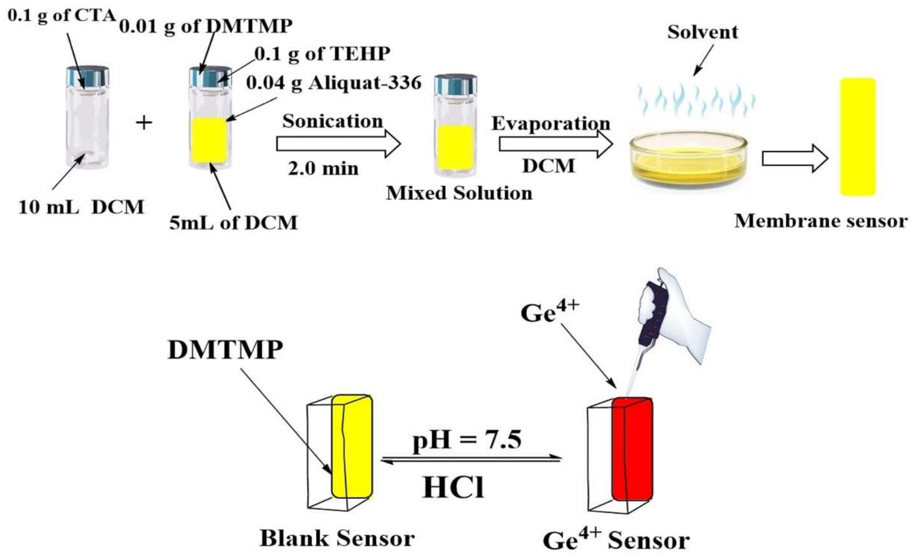
The stoichiometry of the Ge^{4+}–DMTMP complex has been investigated using both the mole continuous-variation and ratio methods. The procedures were carried out at pH 7.50 using Ge^{4+} and DMTMP at a concentration of 5.00×10^{-4} M.

Interference studies

The effect of various interfering cations, including certain alkali metals, transition elements, and lanthanides, on the uptake of Ge^{4+} by the optode was examined by equilibrating optode samples in a borate buffer solution at pH 7.50, each containing a constant concentration of Ge^{4+} and varying concentrations of the interfering cations. The absorption of Ge^{4+} was determined by comparing the absorbance of solutions before and after the optode samples reached the equilibrium.

Application to real samples

The proposed method was used to determine Ge^{4+} ion concentrations in real soil and water samples obtained from



Scheme 2 Schematic representation for the preparation and complexation of the proposed sensor and the Ge^{4+}–DMTMP complex.

industrial sites in and around Quesna and Shoubra. The previously described procedure was use for the analysis of 20.0 mL samples of various water types—including process, natural, seawater, wastewater, and post-oil extraction water—and for an acid-digested soil sample.

Procedure for soil analysis

Soil specimens were taken from manufacturing areas in the cities of Shoubra and Quesna. These samples were air-dried in a laboratory oven at 70.0 °C, then finely ground and sieved through a 0.25 mm nylon to ensure uniform particle size. A 1.00 g soil sample was subjected to 10.0 mL of concentrated HCl and 3.00 mL of concentrated HNO_3, and then left to stand overnight.[51] The digested product was pH adjusted to 7.50 using borate buffer solution, and then volumetrically standardized in a 25.0 mL graduated flask. The solutions were further processed as shown in the procedure described above.

Determination of germanium in foods

All the samples of food and fruit were purchased from supermarkets located in Benha City. Dry ashing and wet digestion are frequently employed for sample decomposition; however, traditional methods of both methods may result in loss of germanium. To mitigate these problems, a reflux setup was chosen for sample digestion. A 5.00 g sample was combined with 20.0 mL of digesting acid ($HNO_3 : H_2SO_4 = 10:1$) in a 250 mL calibrated flask fitted with a reflux apparatus. The flask was left to stand overnight, then the mixture was gently heated on an electrical heater. After removing the NO_2, the stopcock was turned and the sample solution was gently heated for approximately 3.00 to 5.00 minutes until sulfuric acid fumes were visible. Afterward, the solution was allowed to cool with the stopcock open, and then it was closed once more. Subsequently, 5.00 mL of 30.0% hydrogen peroxide was gradually added while maintaining mild heat. The stopcock was closed, and the mixture was concentrated to roughly 10.0 mL. Finally, the contents were transferred to a 25.0 mL volumetric flask and diluted to the mark with distilled water. The volume of 5.00 mL was pH-adjusted to 7.50, and then volumetrically standardized in a 25.0 mL graduated flask. The solutions were further processed as shown in the procedure described above.

Results and discussion

Measurement principle

DMTMP, bound to the surface of the triacetylcellulose membrane, has been observed to form a complex with Ge^{4+} ions in the borate buffer solution. In this study, DMTMP was incorporated into a CTA matrix which was plasticized using TEHP. No significant color change was observed, when this optode sample was equilibrated with Ge^{4+}-containing solutions across a pH range of 3.00 to 10.0. The absorbance readings of the equilibrated optode samples revealed no evidence of Ge^{4+} ion uptake in the optode containing only DMTMP. This suggests that the DMTMP, immobilized within the TEHP-plasticized CTA matrix, did not exhibit any interaction with Ge^{4+} ions present in the equilibration medium. Aliquat-336 in the optode was observed to enhance the movement of Ge^{4+} from aqueous phase to optode matrix, and its preconcentration as DMTMP–Ge^{4+} complex in the optode. Multivariate optimization and contribution of variables are calculated and explained as follows.

Effect of variable parameters

The selectivity and sensitivity imparted by a given ionophore are known to be strongly influenced by factors such as the membrane composition, nature of the solvent mediator, and the additives used.[52] It was therefore examined in detail the various parameters—including the type of plasticizer, the amount of ionophore, and the incorporation of Aliqout 336—affect the response properties of the membrane.

To determine the optimal DMTMP loading, membranes containing 1.00–8.00 mg of DMTMP were prepared. As the DMTMP amount increased from 1.00 to 4.00 mg, the optodes absorbance increased correspondingly; however, further additions up to 8.00 mg resulted in negligible changes in absorbance (Fig. 2). Therefore, the amount of DMTMP in the optode was set at 4.00 mg for subsequent investigations.

To enhance the optical properties, the quantity of DMTMP incorporated in the optode has been optimized and kept at a constant level. The TEHP-based optode showed more uniformity and superior kinetic performance relative to other plasticizer such as DOP and NPOE. The ratios of TEHP, CTA, and Aliquat-336 within the optode were adjusted to improve uptake efficiency, mechanical strength, response kinetics, and homogeneity. The ideal formulation of the optode was identified as: TEHP = 40.0 wt%, CTA = 40.0 wt%, Aliquat-336 = 16.0 wt%, and DMTMP = 4.00 wt%.

Spectrophotometric analysis was used to investigate the extraction efficiency of Ge^{4+} ions from aqueous solutions by means of the developed optode, revealing a quantitative uptake at pH > 6.00. The sorption kinetics of Ge^{4+} were significantly faster in deionized water (25.0 min) and a borate buffer solution at pH 7.50 (5.00 min). This is because Ge^{4+} may form hydrated

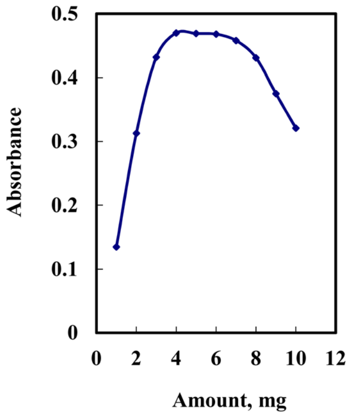


Fig. 2 Absorbance as a function of the amount of DMTMP in the sensor matrix having a fixed proportion of CTA (40.0 mg), TEHP (40.0 mg) and Aliqout 336 (16.0 mg).

species of Ge^{4+} or $GeOH^{4+}$ in an aqueous phase within a pH interval of 6.00–8.00. The presence of quaternary ammonium salts in the optode matrix would impede the sorption of these Ge^{4+} species. Ge^{4+} can form either an anionic or neutral complex with borate, which is readily sorbed into the optode matrix. The optode designed in this method is well-suited for analyzing environmental water samples, as they naturally contain borate ions. The effects of different pH-containing borate buffer solutions on the absorbance of the Ge^{4+} optode at wavelength 545 nm associated with Ge^{4+}–DMTMP complex were further investigated by equilibrating the optode samples for 5.00 min in a solution containing differing levels of buffer and a fixed concentration of Ge^{4+} (100 ng mL^{-1}) at pH 7.50.

The uptake of Ge^{4+} in the optode sample increased with the buffer volume in the equilibrating solution, reaching a maximum at 2.50 mL, after which it stable. At pH 7.50 (0.05 M of both boric and sodium borate), DMTMP is expected to be predominantly present in the optode as HL. This species may form an ion pair with Aliquat-336, facilitating Ge^{4+} extraction. The uptake mechanism can be described by the following reaction:

$$4HL + Ge^{4+} \leftrightarrow GaL_4 + 4H^+$$

where L is the deprotonated form of DMTMP.

Fig. 3 displays the UV-Visible absorption spectra of the blank optode and of optode samples containing different concentrations of Ge^{4+} ions. The figure shows that the blank optode exhibits a peak absorbance (λ_{max}) at 367 nm, which is attributed to the unbound form of DMTMP. Upon interaction with Ge^{4+} ions, the optode samples showed a significant red shift in absorbance, moving from 367 nm (in the absence of Ge^{4+}) to 545 nm, accompanied by an isosbestic point at 453 nm. The absorbance at the maximum wavelength (λ_{max} = 545 nm) increased in direct correlation to the amount of Ge^{4+} accumulated by the optode. This behavior demonstrates that the optodes response is linearly dependent on the concentration of Ge^{4+} ions absorbed from the surrounding solution. In order to evaluate the practical usefulness of the optode for the detection of Ge^{4+}, it was subjected to environmental water samples artificially enriched with Ge^{4+}.

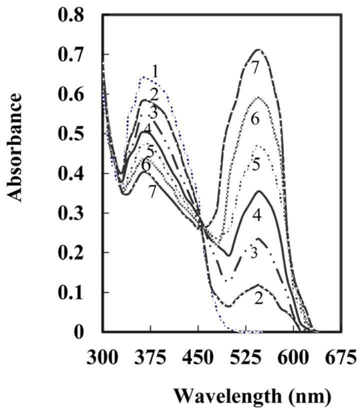


Fig. 3 Absorption spectra of 1-control sensor 2–7 DMTMP optode at 25.0, 50.0, 75.0, 100.0, 125.0 and 150.0 ng mL^{-1} at pH 7.50.

Stoichiometric ratio of Ge^{4+}-DMTMP complex

The absorption spectra of DMTMP and its germanium complex (Ge-DMTMP) were documented at the early stages of the investigation, as shown in Fig. 3. The graph shows that DMTMP has its maximum absorption at 367 nm, while the Ge-DMTMP complex shows a distinct peak at a much higher wavelength of 545 nm. To determine the exact ratio of DMTMP to Ge^{4+} in the complex, we utilized two approaches: the Job's process and the molar ratio process. According to Job's method, the maximum absorption occurred at a DMTMP : Ge^{4+} ratio of 4 : 1. Similarly, the molar ratio method showed an intersection point at a mole ratio of 4, which confirmed the result. Both methods consistently indicated a stoichiometric ratio of 1 : 4 between germanium and DMTMP in the Ge-DMTMP complex. In addition, by comparing the infrared (IR) spectra of DMTMP and the Ge-DMTMP complex, the researchers derived the structural model of the complex, shown in Scheme 3. The conditional formation constant ($\log K$), calculated by Harvey and Manning equation[53] using the data obtained from the above two methods, was found to be 7.35, whereas the true constant was 10.10.

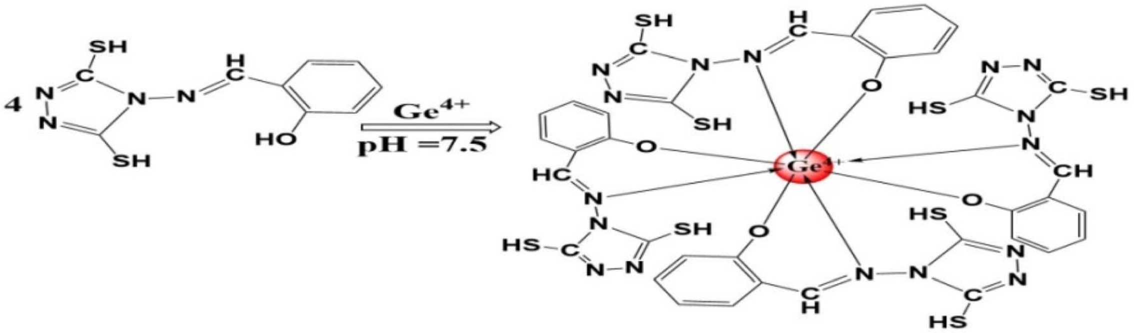
Effect of stirring

The stirring of the Ge^{4+} solution has a significant impact on the sensor's response. Compared to the unstirred solution, stirring resulted in almost three times the improvement. This behavior is attributed to the migration of Ge^{4+} ions towards the fixed DMTMP. The stirring process enhances both the interaction between Ge^{4+} ions and DMTMP and the diffusion of Ge^{4+} ions across the membrane toward DMTMP. In contrast, the absence of stirring, the concentration gradient is the only factor affecting the diffusion of the Ge^{4+} ions through the membrane.[52]

Response time and reusability

The optode's response time to Ge^{4+} was observed to vary with the thickness of the optode sample. The period needed for the optode strip (2 cm × 1 cm) to reach peak absorbance at λ_{max} = 545 nm for the Ge^{4+}–DMTMP complex in a well-agitated Ge^{4+} solution significantly decreased—from 25.0 minutes to just 5.00 minutes—when the optode thickness was reduced from 75.0 μm to 38.0 μm. A decrease in thickness has been observed with respect to the mechanical strength of the self-supporting optode. The ideal equilibration durations for effective Ge^{4+} uptake by the optode sample (with a thickness of 40.0 μm) were determined to be 25.0 minutes from deionized water and 5.00 minutes from an aqueous solution containing 2.50 mL of borate buffer at pH 7.50. The sorption kinetics of Ge^{4+} remained consistent across concentrations spanning from 6.00 to 174 ng mL^{-1} in well-mixed aqueous samples.

Since the optode proposed in this study is capable of preconcentrating Ge^{4+} ions from aqueous solutions, several factors influence its detection limit and applicable concentration range



Scheme 3 The stoichiometric ratio of the formed Ge-DMTMP complex.

for the quantitative analysis of Ge^{4+}. These include the volume of the solution used during equilibration, the minimum quantity of Ge^{4+} needed within the optode matrix to generate a measurable analytical signal, and the sorption capability of the optode toward Ge^{4+}. The experimental findings revealed that a 2 cm × 1 cm optode strip could adsorb up to 88.0 μg of Ge^{4+} ions. The lowest detectable concentration of Ge^{4+} required for a measurable response was determined to be 12.0 μg.

A direct linear correlation was observed between the absorbance at 545 nm and the Ge^{4+} concentration in the aqueous solution, ranging from 6.00 to 174 ng mL^{-1}. Detection capabilities were established through statistical evaluation of blank measurements, where LOD ($3\ \sigma r/s$) and LOQ ($10\ \sigma r/s$) were found to be 1.75 and 5.75 ng mL^{-1}, respectively, with σr denoting blank signal variability and s representing the calibration curve's slope.[54] A comparable response was achieved after 5.00 minutes of equilibration in the presence of borate buffer. The absorbance measurements for optode samples exposed to a constant amount of Ge^{4+} exhibited reproducibility within a margin of 1.00–2.00%. The stability tests of the sensor under different conditions such as atmospheric storage, extreme pH and high-salinity conditions showed that the sensor membrane was not affected the determination Ge^{4+} ions, which further strengthens the reliability of the sensor in real-world environments.

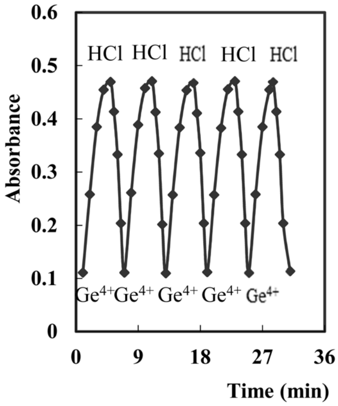


Fig. 4 Reversibility of the sensor exposed 100.0 ng mL^{-1} Ge^{4+} and 0.15 M HCl.

The optode's reusability was evaluated by performing five consecutive cycles of Ge^{4+} sorption and desorption. The desorption of Ge^{4+} from the optode was performed using a 0.15 M HCl solution. Both the sorption and desorption processes were examined by measuring absorbance at 545 nm. Fig. 3 shows the patterns observed over five successive cycles of Ge^{4+} sorption and desorption. Fig. 4 shows that the sorption profile lasted for 5.00 minutes, whereas Ge^{4+} was quantitatively desorbed from the optode in just 2.00 minutes when equilibrated in a well-stirred 2.50 mL aqueous solution of 0.15 M HCl. This demonstrates the reusability of the optode in the proposed method. A schematic representation of the preparation, complexation and regeneration of the proposed sensor and the Ge^{4+}–DMTMP complex is described in Scheme 2 for SI to improve reproducibility.

Finally, the optode was used for analyzing environmental water samples spiked with different concentrations of Ge^{4+}. Some samples in a volume of 2.50 mL had Ge^{4+} a concentration exceeding the analytical range's upper limit. Two sets of experiments were conducted to address this: one employing the samples as obtained and another with 10-fold diluted samples. The pH of the liquid samples was adjusted to 7.50, followed by the addition of 2.50 mL borate buffer solution. The optode samples were then equilibrated with agitation for 5.00 minutes. The mean levels of Ge^{4+} detected in five distinct surface water samples ranged between 12.1 and 30.7 ng mL^{-1}, with relative standard deviations ranging from 1.75% to 2.15%.

Lifetime and stability

The refined membrane retained structural integrity after three weeks of inactivation and showed excellent stability with less than a 1.00% variation in dynamic range during Ge^{4+} ion solution measurements. For the next two months, the optode was exposed daily for one hour to a Ge^{4+} solution (100.0 ng mL^{-1}), during which the optical membrane exhibited only a slight absorbance variation, not exceeding 3.25%. A straightforward rinse with distilled water effectively restored the membrane function. It is noteworthy that no ligand leaching was detected in the solution during the analysis of the samples at this time. This increased stability is probably due to the high lipophilicity of DMTMP and its electron delocalization, both of

Table 1 Impact of interfering ions on the estimation of 100.0 ng mL^{-1} Ge^{4+} at pH 7.50 borate buffer solution

Foreign ions	Added as	Amount tolerated	Foreign ions	Added as	Amount tolerated
K^+	KCl	15 000	La^{3+}	$LaCl_3$	2000
Na^+	$NaNO_3$	13 500	Ti^{2+}	$TiCl_2$	1750
Li^+	LiCl	12 000	Mn^{2+}	$MnCl_2 \cdot 4H_2O$	1500
Ag^+	$AgNO_3$	11 000	Sc^{3+}	$Sc(NO_3)_3$	1300
Ca^{2+}	$CaCl_2$	10 000	Y^{3+}	YCl_3	1200
Ba^{2+}	$BaCl_2 \cdot 2H_2O$	9250	Cr^{3+}	$CrCl_3$	1100
Mg^{2+}	$MgCl_2$	8500	Se^{4+}	Na_2SeO_3	1000
Cd^{2+}	$CdCl_2$	8000	Zr^{4+}	$ZrCl_4$	925
Co^{2+}	$CoCl_2 \cdot 6H_2O$	7500	Pt^{4+}	$PtCl_4$	850
Cu^{2+}	$CuCl_2 \cdot 6H_2O$	7000	Te^{4+}	Na_2TeO_3	825
Zn^{2+}	$ZnCl_2$	6500	Sn^{4+}	$SnCl_2 \cdot 2H_2O$	800
Sn^{2+}	$SnCl_2 \cdot 2H_2O$	6000	Th^{4+}	$ThCl_4$	800
Fe^{2+}	$FeSO_4$	5500	$UO_2{}^{2+}$	$UO_2(NO_3)_2$	800
Sr^{2+}	$SrCl_2$	5000	Ce^{4+}	$Ce(NO_3)_4$	800
Pb^{2+}	$PbSO_4$	4500	V^{5+}	V_2O_5	800
Pd^{2+}	$PdCl_2$	4000	Cr^{6+}	$K_2Cr_2O_7$	775
Ni^{2+}	$Ni(NO_3)_2 \cdot 6H_2O$	3500	Mo^{6+}	$(NH_4)_2Mo_7O_{24} \cdot 2H_2O$	775
Hg^{2+}	$HgCl_2$	3000	W^{6+}	Na_2WO_4	775
Al^{3+}	$AlCl_3$	2500	Os^{8+}	OsO_4	750
Fe^{3+}	$FeCl_3$	2250			

which increase the durability of the system when complexed with Ge^{4+} ions.

Inter-day and intra-day precision

Reproducibility, assessed over several days, and repeatability, assessed over one day, were assessed by performing five consecutive extraction and determination procedures with 100 ng mL^{-1} of Ge^{4+}. For the intra-day assessment, the tests were conducted within the same day, while for inter-day assessment the tests were spread over three consecutive days. Both assays produced satisfactory results, with a relative standard deviation

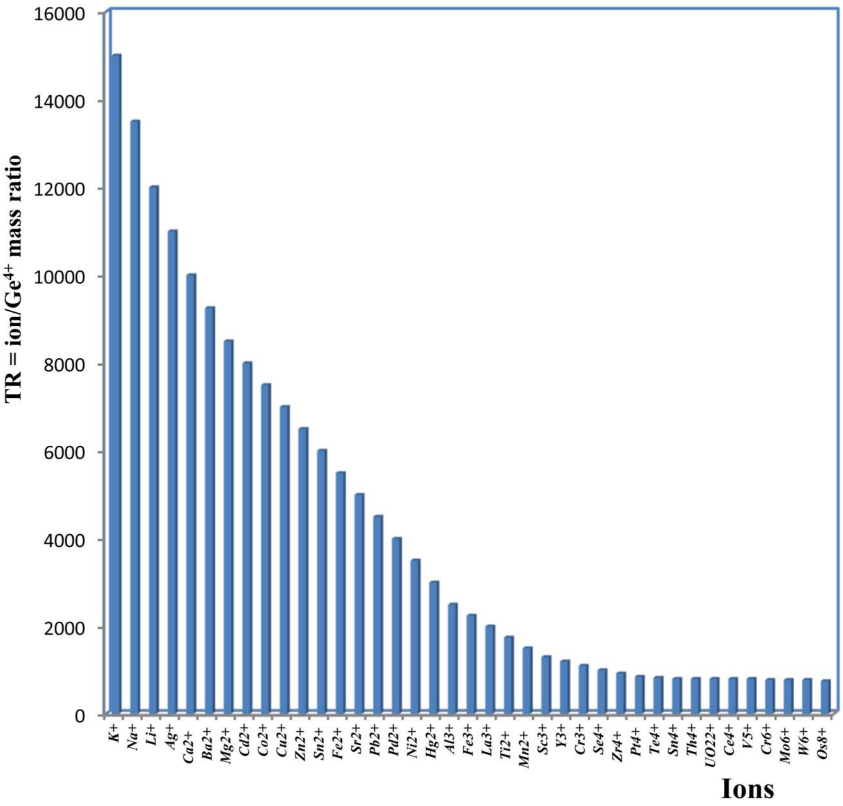


Fig. 5 Tolerance ratio for various interfering ions in the determination of 100.0 ng mL^{-1} of Ge^{4+}.

(%RSD) of 1.93 for intra-day and 2.25 for the inter-day measurements, respectively.

Accuracy/recovery

Assessment of accuracy is necessary to validate any analytical procedure. In this context, samples like distilled water and municipal water, which were initially free of Ge^{4+}, were enriched with the analyte to measure the accuracy. The Results from different applications of the proposed procedure consistently ranged from 98.70% to 101.80%. This consistency confirms the procedures accuracy and underscores its lack of interference from other ions.

Table 2 Survey of spectrometric methods applied for the determination of germanium

Spectrophotometric reagent	Beer's law ($\mu g\ mL^{-1}$)	LOD[a] ($\mu g\ mL^{-1}$)	Selectivity	Analyzed sample	Ref.
Phenylfluorone and zephiramine[b]	47.5	0.10	$Sn^{2+,4+}$, Sb^{3+}, Ta^{5+}, Nb^{5+}, W^{6+}, Mo^{6+}	Ground water	55
Nano-sized TiO_2[c]	43.0		Sr^{2+}, Zn^{2+}, PO_4^{3-}, F^-	Water	56
Nano-TiO_2 (salicyl fluorone in the presence of cetyltrimethylammonium bromide)[b]	0.0–0.24	0.072	Si^{4+}, Sn^{4+}, Al^{3+}, Fe^{3+}	Water; certified reference material	57
Preconcentration on an organic solvent-soluble membrane and determination with *o*-nitrophenylfiuorone in presence of sodium dodecyl sulfate [b]	0.02–0.36	0.004	Pb^{2+}, Mo^{6+}	Chinese herb, waters, and urine sample	58
Phenylfluorone[b]			Sb^{3+}, Sb^{5+}, Sn^{2+}, Mo^{6+}, Ti^{4+}	Lignite ashes	59
Phenylfluorone[b]	0.01–0.06	0.005	In^{3+}, Fe^{2+}, Te^{4+}, Tl^{+}, Sn^{4+}		60
TiO_2 nanoparticles (salicyl fluorone in the presence of cetyltrimethylammonium bromide)[b]			Cu^{2+}, Ba^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Se^{4+}, Sr^{2+}, Li^{+}, Si^{4+}		61
9-(*o*-Chlorophenyl)-2,6,7-trihydroxyxanthen-3-one (cetyltrimethyl ammonium bromide)[b]	0.0–200		Ba^{2+}, Pb^{2+}, Ga^{3+}, Sb^{3+}, V^{5+}, Cr^{6+}, W^{6+}, Mo^{6+}	Minerals & ores	60
Coprecipitation of germanium in the presence of Mg^{2+}, Ga^{3+}, Ca^{2+} and HCO_3^- [d]		0.006		Sea-, surface- and ground-waters	64
Precipitation with $Fe(OH)_3$ and determination with trimethoxylphenylfluorone[b]	0.0–0.24	0.021	Sr^{2+}, Pb^{2+}, Zr^{4+}, Ti^{4+}, Mo^{6+}	Foods	32
The separation was doned by an isocratic elution[e]	0.05–5.0			Tonic oral liquids	65
Catechol violet and cetyltrimethylammonium bromide[b]	0.1–1.0		Sn^{4+}, Fe^{3+}, Bi^{3+}, V^{5+}, Cr^{6+}, Mo^{6+}, Sb^{3+}		65
Mercapto-modified silica gel[e]	0.01–0.20	0.008	Co^{2+}, Cu^{2+}, Ni^{2+}		66
Cloud point methodology, triton X-114[f]	10–300	0.59	As^{4+}, Te^{4+}, Sb^{4+}	water samples	12
Chitosan functionalized with di-2-propanolamine[g]	50	0.002		Seawater samples	67
Modified copolymer styrene-maleic anhydride, (bis(2,3,4-trihydroxyphenyl-azo) benzidine in the presence of heterocyclic amines)	0.0–90	0.18	Cu^{2+}, Fe^{3+}	Seawater obtained after oil pumping	68
(Methybenzeneazosalicylfluorone) using ultrasound-assisted leaching[b]	2.75	0.007	Cr^{3+}, Hg^{2+}, Ti^{4+}, U^{6+}, As^{3+}, Bi^{3+}), Se^{4+}, Te^{4+}, Pt^{4+}, Pt^{2+}, Pd^{2+}, Ln^{3+} Ru^{4+}, Au^{3+}	Certified reference materials	34
Anionic resin (IRA-900), catechol[h]				Fly ash	69
Kelex-100, [7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline] functional sol gel[i]			As^{3+}, Sb^{3+}, Zn^{2+}, Ni^{2+}	Water	70
Preconcentration/separation procedure (spectrophotometric reagent) pyrogallol[i]	12–90	0.018	As^{3+}, Sn^{4+}	Ore	71
2-Amino-4-(*m*-tolyazo)pyridine-3-ol at pH 3.5-Triton X-100 and KCl, immobilized on chitosan[j]	0.5–75	0.017		Water	72
(DMTMP) sensor[b]	0.00175	0.006–0.174	Highly selective	Water and food	This work

[a] LOD: Limit of detection technique. [b] spectrophotometery. [c] Graphite furnace atomic absorption. [d] Hydride generation-atomic. [e] High-performance ion-exclusion chromatography. [f] Hydride generation flame atomic absorption spectrometry. [g] Inductively coupled plasma mass spectrometry. [h] Atomic absorption spectrometry. [i] Adsorptive stripping voltammetric; spectrometry; emission spectrometry. [j] Flow injection hydride generation atomic fluorescence spectrometry.

Robustness and ruggedness

The robustness of the techniques was assessed by measuring absorbance values at different wavelengths. At the same time, method ruggedness was confirmed by having two different researchers perform the procedure and by a single analyst using two different cuvettes. The consistent results achieved from these tests fell within an acceptable range, underscoring the reliability and stability of the procedures.

Interferences study

To evaluate the influence of competing cations, calibration curves for the membrane were generated in the occurrence of potential interfering ions, like K^+, Ag^+, Na^+, Li^+, Pb^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, Sr^{2+}, Zn^{2+}, Mg^{2+}, Ba^{2+}, Fe^{3+}, Fe^{3+}, Al^{3+}, Cr^{3+}, La^{3+}, Cr^{3+}, Sc^{3+}, Se^{4+}, Te^{4+}, Th^{4+}, and UO_2^{2+}. Table 1 and Fig. 5 collectively highlight that the optode shows minimal interference from other ions, while displaying a pronounced sensitivity specifically to Ge^{4+}.

Selectivity describes the sensor's preference for responding to the target ion over other potentially interfering ions. Table 1 demonstrates the film's selectivity for the maximum tolerance ratio to Ge^{4+} ion, at 15 000-fold higher concentration of interfering ions compared to the primary ion (Ge^{4+} at 100.0 ng mL^{-1}). According to the table, all the tested ions show acceptable tolerance levels, at a concentration of 750 times (for Os^{8+}) higher than that of Ge^{4+} in the solution.

Comparison with other studies

In contrast to earlier approaches for the preconcentration and spectro-photometric detection of Ge^{4+}[12,13,33,35,55–72] (Table 2), the proposed optode provides greater simplicity, faster analysis, and lower detection limit. Although the method described[68] in—employing a modified styrene-maleic anhydride copolymer along with bis(2,3,4-trihydroxyphenyl-azo) benzidine in the occurrence of heterocyclic amines and spectrophotometric detection—exhibits similar selectivity, the proposed procedure offers lower detection limits and a narrower determination range. The proposed method offers greater advantages in terms of sensitivity and interference resistance. To the best of our knowledge, this study represents the first reported use of DMTMP as a chromogenic reagent for the preconcentration and optical sensor-based determination of Ge^{4+}.

Compare the advantages of the proposed method to existing optical sensors, the present method provides a simple and cost-effective method for preconcentrating, extracting and determining the concentrations of Ge^{4+} ions without interference

Table 3 Results of the determination of Ge^{4+} in various water samples ($n = 6$; $P = 0.95$)

		Proposed method		ICP-AES method			
Sample	Ge^{4+} added ng mL^{-1}	Found[a]	Recovery (%)	Found[a]	Recovery (%)	*t*-test[b]	*F*-test[c]
Process water	0.00	—		—			
	40.0	39.8 ± 0.56	99.6	40.6 ± 1.76	101.5	1.06	
	80.0	80.5 ± 0.73	100.6	79.0 ± 1.49	98.8		2.11
	120.0	121.2 ± 0.47	101.0	118.2 ± 1.52	98.5	0.72	
Natural water	0.00	—		—			
	60.0	60.4 ± 0.81	100.7	59.3 ± 1.36	98.8		3.76
	120.0	119.0 ± 0.39	99.2	121.8 ± 1.84	101.5	1.76	
	180.0			183.2 ± 1.71	101.8		
Waste water	0.00	—		—			
	35.0	35.4 ± 0.74	101.1	34.4 ± 1.28	101.2	1.35	
	70.0	69.1 ± 0.61	98.7	70.9 ± 1.53	101.3		3.59
	140.0	141.6 ± 0.93	101.1	138.3 ± 1.75	98.8	1.81	
Sea water[d]	0.00	12.1	—	12.0	—		
	25.0	36.8 ± 0.81	99.2	38.2 ± 1.97	103.2		2.66
	50.0	63.2 ± 0.97	101.8	60.9 ± 1.42	98.2	0.82	
	60.0	71.4 ± 0.90	101.0	73.4 ± 1.48	101.9		1.98
Water obtained after oil pumping[e]	0.00	30.7	—	30.5	—		
	15.0	45.2 ± 0.87	101.4	44.5 ± 1.66	97.8		3.13
	30.0	60.0 ± 0.91	98.8	61.4 ± 1.48	101.5	1.66	
	45.0	76.1 ± 1.38	100.5	74.1 ± 1.74	98.2		3.73
Soil[f]	0.00	26.5	—	26.2	—		
	40.0	65.8 ± 0.65	98.9	67.8 ± 1.81	102.4	1.90	
	80.0	108.2 ± 0.87	101.6	104.9 ± 1.48	98.5		3.75
	120.0	145.0 ± 1.02	99.0	148.3 ± 1.77	101.4	1.87	
Soil[g]	0.00	12.3	—	12.4	—		
	20.0	31.9 ± 0.76	98.8	33.0 ± 1.84	101.9		3.67
	40.0	52.8 ± 0.92	101.0	51.6 ± 1.43	98.5	1.95	
	60.0	71.7 ± 0.81	99.3	73.3 ± 1.29	101.2		3.83

[a] Mean ± relative standard deviation ($n = 6$). [b] Tabulated *t*-value for five degrees of freedom at P (0.95) is 2.57. [c] Tabulated *F*-value at P (0.95) is 5.05. [d] Mediterranean sea from Alexandria. [e] Water obtained after oil pumping (Red sea from El-Ghardaka). [f] Obtained from Shoubra City. [g] Obtained from Quesna City.

from most cations and anions present in the real samples. The comparative data show significant improvements in the performance of the current sensor, in particular in terms of its faster response time, reduced interference susceptibility, improved qualitative, and diagnostic capability, extended linear range, and more efficient processing compared to previous designs.

Reproducibility and repeatability

The main key characteristics of a sensor are its reproducibility and repeatability. The sensor membrane's repeatability was evaluated by submerging it multiple times in solutions with 100.0 ng mL^{-1} Ge^{4+} ions. After ten measurements, the relative standard deviation of the absorbance values recorded at λ = 545 nm in the Ge^{4+} solution was around 1.93%, demonstrating consistent performance of the sensor.

The reproducibility of the sensor membranes was assessed by determining the absorbance of a 100.0 ng mL^{-1} Ge^{4+} solution through six different membranes. The relative standard deviation of the absorbance values recorded at $\lambda = 545$ nm in the Ge^{4+} solution was around 2.25%. These results confirm the excellent reproducibility and repeatability of the sensor membrane.

Analytical applications

The optode developed for Ge^{4+} detection was used for the analysis of water and seawater samples collected post oil extraction. The results, when compared to results obtained with the standard ICP-AES technique, demonstrated the proposed method's high precision and accuracy (Table 3). The studied water samples contained germanium at concentrations of several tens of ng L^{-1}.[1,11]

Germanium concentration was increased by a factor of 200 during the treatment process. In addition to, known quantities of Ge^{4+} were spiked into the water samples prior to pretreatment. There was strong agreement among the estimated and added amounts of Ge^{4+}, and excellent recoveries were achieved, demonstrating the sorbent's effectiveness for selectively extracting germanium from different water samples. The effectiveness of the suggested method was evaluated by determining the *t*-value (for accuracy) and conducting an *F*-test (for precision) in comparison to the ICP-AES technique. The average values were derived using Student's *t*-tests and *F*-tests with a 95.0% confidence level and five degrees of freedom.[73] The results showed that the calculated values (Table 3) were within the theoretical limits. Compared to the alternative method, the proposed approach shows superior accuracy, wider detection

Table 4 The results of the determination of germanium in food and fruit samples

		Ge content^a (ng g^{-1})		Recovery (%)			
Samples	Spiked (ng g^{-1})	Proposed	ICP-AES	Proposed	ICP-AES	*t*-test^b	*F*-test^c
Bean	—	71.3 ± 0.16	70.9 ± 0.87	—	—		
	20.0	90.7 ± 0.32	92.5 ± 1.16	99.3	101.8	1.78	
	40.0	111.0 ± 0.27	113.0 ± 1.21	99.7	101.9		3.53
Rice	—	11.2 ± 0.31	11.0 ± 1.23	—	—		
	35.0	46.5 ± 0.45	45.4 ± 1.49	100.7	98.7	1.88	
	70.0	80.8 ± 0.58	83.4 ± 1.62	99.5	103.0		3.92
Egg	—	53.5 ± 0.09	53.8 ± 1.05	—	—		
	15.0	69.1 ± 0.16	67.7 ± 1.17	100.9	98.4	1.67	
	30.0	84.5 ± 0.28	85.3 ± 1.25	101.3	101.8		3.74
Cornmeal	—	16.0 ± 0.24	15.7 ± 1.47	—	—		
	50.0	65.2 ± 0.37	67.5 ± 1.54	98.8	102.7	1.53	
	100.0	118.4 ± 0.41	114.7 ± 1.37	102.1	99.1		3.77
Apple	—	13.2 ± 0.39	13.5 ± 1.29	—	—		
	60.0	73.8 ± 0.31	71.9 ± 1.46	100.8	97.8	1.79	
	120.0	135.7 ± 0.22	131.6 ± 1.39	101.9	98.6		4.04
Chicken	—	25.6 ± 0.13	26.0 ± 1.56	—	—		
	25.0	50.0 ± 0.33	51.8 ± 1.71	98.8	101.6	1.85	
	50.0	76.5 ± 0.13	75.4 ± 1.82	101.2	99.2		3.97
Sunflower oil	—	43.3 ± 0.25	43.7 ± 1.63	—	—		
	27.5	71.7 ± 0.09	69.7 ± 1.15	101.3	97.9	1.66	
	55.0	99.9 ± 0.16	99.4 ± 1.07	101.6	100.7		3.49
Peach	—	21.6 ± 0.42	21.5 ± 0.93	—	—		
	70.0	90.8 ± 0.24	92.8 ± 1.35	99.2	101.4	1.71	
	140.0	160.3 ± 0.31	163.2 ± 1.62	99.2	101.1		3.68
Tea	—	14.1 ± 0.26	14.0 ± 1.33	—	—		
	65.0	80.0 ± 0.37	67.9 ± 1.67	101.1	98.4	1.95	
	130.0	143.6 ± 0.44	145.7 ± 1.38	99.7	101.2		4.22
Butter	—	21.7 ± 0.11	21.5 ± 1.46	—	—		
	55.0	77.4 ± 0.19	75.6 ± 1.53	100.9	98.8	1.78	
	110.0	133.0 ± 0.30	129.9 ± 1.71	101.0	98.8		3.82

[a] Mean ± S.D. ($n = 6$). [b] Tabulated *t*-value for five degrees of freedom at *P* (0.95) is 2.57. [c] Tabulated *F*-value at *P* (0.95) is 5.05.

range, enhanced stability, and reduced time requirements, highlighting its overall benefits.

Determination of germanium in food and fruit samples

The practical application of the fabricated optode has been demonstrated by the detection of trace levels of Ge^{4+} in various samples of food and fruit. To confirm the method's accuracy, spiking tests and separate analytical procedures were conducted, and the findings are summarized in Table 4. For comparison, AAS was used as a reference process, with its results also presented in Table 4. The recovery of spiked samples showed reasonable accuracy, which was further confirmed by the standard addition method, demonstrating the system's effectiveness in ion detection. A strong correlation between the spiked and detected amounts of the analyte was observed. As shown in Tables 3 and 4, the germanium concentrations determined using the developed method closely matched those obtained by ICP-AES. Recovery rates for the added standards consistently surpassed 95.0%, strongly supporting the method's precision and its reliability regardless of matrix interferences.

Conclusions

The color-changing optode for detection of Ge^{4+} ions in aqueous samples was produced by immobilization of DMTMP and the liquid ion-exchanger Aliquat-336 in a matrix of tri-(2-ethylhexyl) phosphate-plasticized cellulose triacetate. The optode showed a linear response after a 5.00 minute equilibration period in a well-stirred borate medium, as well as under comparable conditions in deionized water. The adsorbed ions of Ge^{4+} in the optode matrix can be quantified by visual colorimetry. The developed optode showed its reusability by releasing Ge^{4+} ions after equilibration in a 0.15 M HCl solution for 2.00 minutes. The presence of cations such as Zn^{2+}, Fe^{2+}, Cu^{2+}, and Pb^{2+} did not significantly interfere with the uptake of Ge^{4+} ions in the optode sample or the subsequent color development. A marked alteration in color and an absorbance exceeding 3σ of the blank were observed in aqueous samples (tap water) containing 11.0 ng in 100 mL (0.11 ng mL^{-1}) after 25.0 minutes of equilibration.

Author contributions

Mostafa Nassar, conceptualization, validation, methodology, investigation, data curation, validation, methodology, formal analysis. Alaa Amin:supervision, conceptualization, validation, writing – review & editing, writing – original draft.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors declare that the data supporting the findings of this study are available within the article.

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