Cumhuriyet Sci. J., 46(4) (2025) 805-811
DOI: https://doi.org/10.17776/csj.1683087

Cumhuriyet Science Journal

| csj.cumhuriyet.edu.tr | Founded: 2002 ISSN: 2587-2680 e-ISSN: 2587-246X Publisher: Sivas Cumhuriyet University

Construction of a New Near-Infrared Cobalt Phthalocyanine Platform for the Selective and Sensitive Detection of Thiocyanate Ions

Ozgur Yavuz[1, a,*]

[1] *Department of Chemistry, Istanbul Technical University, 34469, Maslak, Istanbul, Türkiye*

**Corresponding author*

Research Article

History
Received: 24/04/2025
Accepted: 09/11/2025

ABSTRACT

Thiocyanate (SCN^-) is an organic anion with various applications; however, it causes serious environmental and health hazards. In this report, a new near-infrared (NIR) chemical sensor based on a phthalocyanine (Pc) platform was devised for the selective, sensitive, and rapid determination of SCN^- ions. To enhance the sensor's longevity, a robust Pc core structure with unique properties was selected. Additionally, a central cobalt (II) ion (Co^{2+}) was incorporated owing to its strong binding affinity for SCN^-, as previously demonstrated in the literature. The macromolecule DAP-CoPc is the first spectrophotometric probe designed for the selective quantification of SCN^- within Pc and porphyrin-based frameworks. The limit of detection (LOD) for the UV–vis titration was determined to be 11.01 µM (0.71 ppm) with a response time of 100 s. Overall, the findings of this study emphasise the exceptional sensing performance of DAP-CoPc, particularly in terms of selectivity, sensitivity, reasonable response time, and durability. This work represents a significant advancement for the development and application of novel NIR sensor platforms for the accurate and fast detection of SCN^- in real samples.

Keywords: Cobalt Phthalocyanine, thiocyanate, UV-vis spectrophotometry, chemosensor, Near-Infrared.

[a] *yavuzozg@itu.edu.tr* *https://orcid.org/0000-0002-0660-7474*

Introduction

In recent years, the excessive release of toxic chemicals and pollutants causes a profound negative impact on the entire ecosystem and has drawn significant attention from the scientific community. Among these pollutants, thiocyanate, an organic anion with toxic properties, is a particularly hazardous byproduct originating from the mining industry, hydrometallurgy, fabric dyeing, car exhaust, and diet [1,2]. Although it has widespread applications, including in medicine, photography, and painting, prolonged exposure to SCN^- ions pose serious health risks, such as anxiety disorders, fatigue, palpitations, and neurological disorders [3,4]. Additionally, cigarette smoke is another major source of thiocyanate exposure, as small amount of hydrogen cyanide present in tobacco smoke are metabolized to SCN^- in the liver [5]. For these reasons, the rapid and reliable determination and monitoring of SCN^- ions are essential to minimize potential adverse health effects.

To date, several analytical techniques have been applied for the detection of thiocyanate, including high-performance liquid chromatography (HPLC) [6], capillary zone electrophoresis [7], voltammetry [8], flow injection amperometry [9], gas chromatography-mass spectrometry [10], and spectrophotometric analysis [1,11]. However, many of these methods exhibit significant limitations, such as high instrumentation costs, time-consuming procedures, the necessity for specialized personnel, and lengthy sample preparation [12]. Among these techniques, spectrophotometry has gained prominence in recent years due to its simple applicability, cost-effectiveness, and ability to provide prompt and reliable results without the need for sophisticated equipment or highly trained operators [13].

On the other hand, a variety of sensor platforms have been utilized in the literature for SCN^- detection. These include potentiometric sensors incorporating materials such as PVC-membrane electrodes [14], crown ether–cetyltrimethyl ammonium thiocyanate [15], tribenzyltin(IV) dithiocarbamate [16], and aryl palladium complexes [17], as well as amperometric sensors employing silver nanoparticle-modified electrodes [18], PVC-membrane electrodes [19], gold-electrodes [20] and magnetite ore (Fe3O4)-based composites [21]. Despite the growing interest in alternative detection strategies, spectrophotometric (UV-vis and fluorometric) methods for SCN^- analysis remain relatively rare [1,11,22,23].

Phthalocyanines are highly stable, conjugated macromolecules that have attracted considerable interest owing to their unique structural and electronic properties [24]. Their two-dimensional, delocalized 18-π electron system surrounding the core enables strong absorption and emission capabilities in the NIR region [25]. In addition to their remarkable thermal, optical, and electrical characteristics, Pcs offer versatile functionalization options at both peripheral and non-peripheral positions, along with a wide range of central metal ions and axial ligands [26]. These features have paved the way for their applications in diverse fields,

including solar cells [27], photodynamic cancer therapy [28], nonlinear optical materials [29], supercapacitors [30], photo-initiating systems [31], and chemical sensors [32].

However, in some cases, the large, conjugated structure of Pcs can result in solubility issues and undesirable aggregation (typically in the H and J types of aggregates) if not properly modified [33,34]. Despite these challenges, careful molecular design and precise fabrication strategies can effectively address these limitations, allowing Pcs to be optimized for specific applications.

In this study, a non-aggregated, electron-rich, octa-substituted cobalt phthalocyanine (DAP-CoPc) incorporating N,N-dimethylaminophenyl units was designed and synthesized via a cyclotetramerization reaction. These functional groups not only improve solubility but also facilitate enhanced electronic delocalization. The macromolecule DAP-CoPc represents the first spectrophotometric probe specifically designed for the sensitive detection of SCN^- in "phthalocyanine and porphyrin-based structures". The probe stands out with its reasonable response time (100 s) and long-term stability, remaining durable for at least two months.

Experimental Section

Reagents and Materials

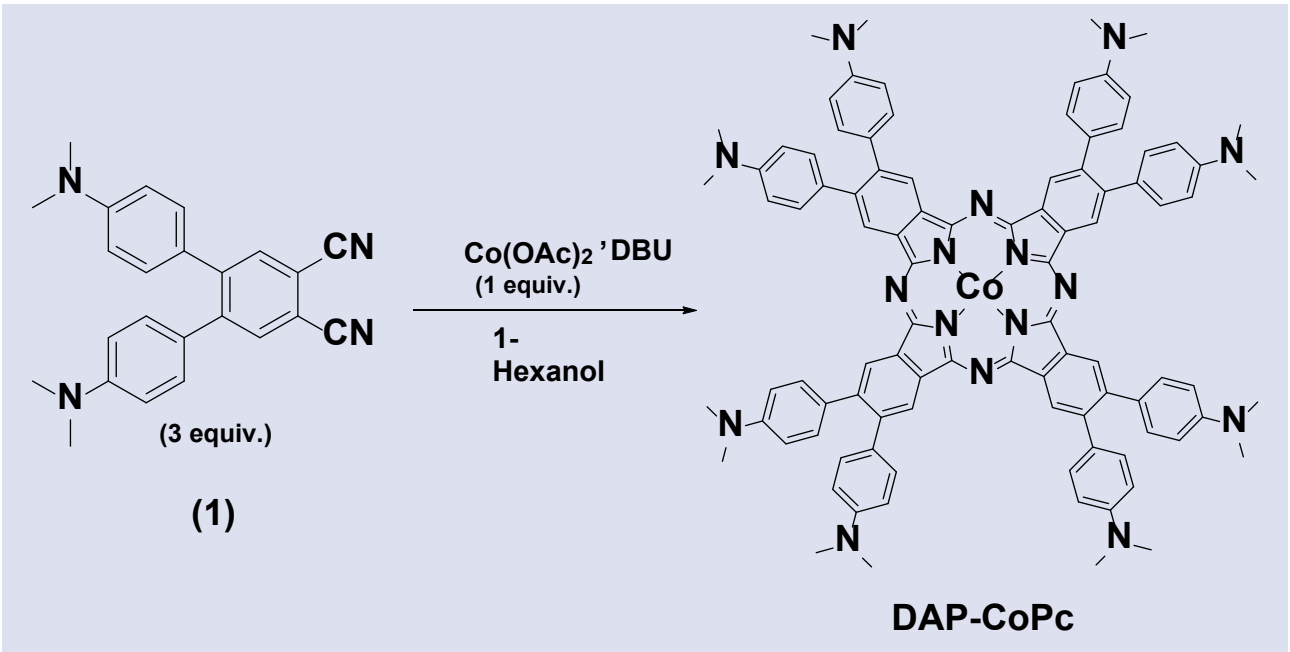
Compound (1) was obtained according to our previous study [34]. Cobalt(II) chloride hexahydrate (98%), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (100%), ethyl acetate (>99.5%), n-hexanol (100%), tetrahydrofuran (THF) (>99.9%), methyl alcohol (MeOH) (>99.8%), hexane (>97%), diethyl ether (>99%), dichloromethane (>99.8%), acetone (>99.5%), and all salts (>99.9%) used in spectrophotometric studies, were supplied from commercial sources and exploited without further purification process.

Instrumentation

Matrix-Assisted Laser Desorption/Ionization–Time of Flight–Mass Spectrometry (MALDI-TOF-MS) analysis was performed via BRUKER Microflex LT instrument with 2,5-Dihydroxybenzoic acid (DHB) as the matrix. UV-vis spectra were obtained on an Agilent 8453 spectrophotometer using 1 cm path length cuvettes at ambient temperature. Infrared spectra were collected with a Perkin–Elmer FT-IR spectrometer.

Synthesis of Phthalocyanine-Based Chemical Sensor for SCN^- Analysis

The synthesis of DAP-CoPc was carried out as illustrated in Scheme 1. A mixture of compound 1 (206 mg, 0.560 mmol), and cobalt(II) chloride hexahydrate (45 mg, 0.189 mmol) dissolved in 1-hexanol (1.5 mL) in a reaction tube was stirred for 30 min in argon atmosphere, and the reaction temperature was arranged to 160 °C. DBU was added, after the temperature reached 120 °C. Then, the tube was securely sealed, and the mixture was continued to stir at 160 °C for 6 hours. The mixture was then allowed to cool in a water-bath. Once the mixture cooled the room temperature, it slowly poured into MeOH. After centrifugation process, the crude solid product was subjected to wash with hot ethyl acetate, hot methanol (MeOH), hot acetone, and finally diethyl ether. The solid product was dried through vacuum oven to yield pure, black-colored DAP-CoPc. (65 mg, 31 %). MALDI-TOF-MS (m/z): calculated for (C96H88N16Co) 1523.67, found [M]+ = 1523.574. FT- IR (ATR): max/(cm-1): 3043, 2923, 1604, 1521, 1434, 1348, 1105, 941, 815, 754, 701, 538.



Scheme 1. Synthesis route of DAP-CoPc.

Measurement Methods

A stock solution of DAP-CoPc (5.0 × 10-4 M) was obtained in THF, and the required solutions were adjusted to the needed conditions based on the specific experimental requirements. Stock solutions of potassium or sodium salts of different anions (5.0 × 10-2 M) were provided using double-distilled water. UV-vis titration and selectivity studies were achieved through a 1.0 × 10-5 M DAP-CoPc solution in THF in a 3 mL quartz cuvette. Measurements were taken by incrementally adding appropriate amounts of aqueous anion salt solutions to the probe solution.

Result and Discussion

Design, Synthesis, Characterization, and Photophysical Properties

During the design phase, the Pc macrocyclic unit was selected as the core structure owing to its exceptional thermal, optical, and chemical stability, which facilitates the development of a robust and durable chemical sensor platform. Functionalization of the Pc framework with *N,N*-dimethylaminophenyl groups was designed to improve solubility, increase electron density within the core, and consequently extend the lifetime of the probe [35]. Additionally, cobalt(II) was selected as the central metal ion due to its strong binding affinity for SCN^- ions. Notably, previous studies have demonstrated that cobalt ions can selectively interact with SCN^- in various designed platforms [1,22,36].

The novel macrocyclic compound DAP-CoPc was synthesized via a cyclotetramerization reaction of compound (1) in refluxing hexanol under an argon atmosphere. The completion of the reaction was affirmed by the disappearance of the nitrile group peak of compound (1) at approximately 2224 cm^{-1} in the FT-IR spectrum, a key indicator of the successful formation of Pc compounds. Following purification, the target product DAP-CoPc was obtained with a satisfactory yield of 31%. Furthermore, the molecular structure of DAP-CoPc was elucidated using various spectroscopic techniques, including UV–Vis, MALDI-TOF mass spectrometry, and FT-IR (Figures S1–S3). Due to the paramagnetic nature of the cobalt(II) ion, characterization by NMR spectroscopy and fluorescence-based spectroscopic analysis could not be performed.

In the mass spectrum (Figure S2), the primary peak at *m/z* 1523.574 is in close agreement with the expected value of 1523.67, providing strong confirmation of the successful synthesis of DAP-CoPc. Moreover, the other fragments at *m/z* 1509.368 and 1494.879 indicate, respectively, the loss of one and two methyl groups from the DAP-CoPc molecule. Furthermore, to confirm the coordination of the Co^{2+} ion within the central cavity, the FT-IR spectra of DAP-CoPc and unsubstituted H_2Pc (nonmetallic form) were compared. In the FT-IR spectrum, the characteristic N–H stretching peak observed in H_2Pc is absent in DAP-CoPc, indicating successful incorporation of the Co^{2+} ion into the central cavity of the phthalocyanine ring (Figure S3). The peak observed around 3350 cm^{-1} is likely attributed to moisture. Although the DAP-CoPc probe was stored in a vacuum oven at high temperature for an extended period, the peak at 3350 cm^{-1} reappeared. This suggests that the DAP-CoPc compound possesses hygroscopic characteristics, leading to the reabsorption of moisture from the environment.

The spectral properties of DAP-CoPc were investigated using UV–Vis spectroscopy. The UV–Vis spectrum of DAP-CoPc in THF is presented in Figure S1, displaying characteristic absorption peaks at approximately 322 nm and 703 nm, corresponding to the B (Soret) and Q bands of DAP-CoPc, associated with $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, respectively.

In certain cases, Pcs are prone to aggregation, which can alter their electronic structure and significantly reduce their effectiveness in various applications. The most commonly observed aggregation type, H-type aggregation, follows a face-to-face (sandwich) arrangement and results in a blue shift of the Q band [33]. Conversely, J-type aggregation, characterized by a head-to-tail configuration, induces a red shift in the Q band [34]. According to the UV–Vis analysis (Figure S1), DAP-CoPc exhibits excellent monomeric behavior, as evidenced by the sharp, unsplit Q band. This monomeric nature is primarily attributed to the non-aggregated form of DAP-CoPc. In addition, the stability of DAP-CoPc over an extended period (two months) without any signs of degradation was confirmed using the UV–Vis spectroscopy method (Figure S4).

Selectivity Investigation Study

The selectivity of DAP-CoPc was evaluated by analyzing its UV–Vis responses in the presence of various anions (F^-, Cl^-, Br^-, I^-, NO_2^-, NO_3^-, CH_3COO^-, SO_4^{2-}, S^{2-}, HSO_4^-, citrate, ClO_3^-, SO_3^{2-}, HCO_3^-, ClO_4^-, $S_2O_5^{2-}$, HS^-, CN^-, SO_3^{2-}, HSO_3^-, PO_4^{3-}, and SCN^-). The addition of various anions caused no notable changes in absorbance at 703 nm, with the only exception being SCN^-. Upon introducing SCN^- into the DAP-CoPc solution, a distinct charge-transfer band appeared at 400 nm, accompanied by a red shift in the Q band from 703 nm to 708 nm (Figure 1). Furthermore, the appearance of distinctive isosbestic points at 336 nm, 363 nm, 679 nm, and 703 nm strongly supports the formation of the DAP-CoPc–SCN complex.

To confirm that the spectral changes were due to the binding of SCN^- ions to the Co^{2+} metal center, the interaction of H_2Pc with all tested anions was also examined (Figure S5). The results showed no observable response of H_2Pc toward any of the anions, indicating that complexation occurs specifically between SCN^- ions and the Co^{2+} ion in DAP-CoPc.

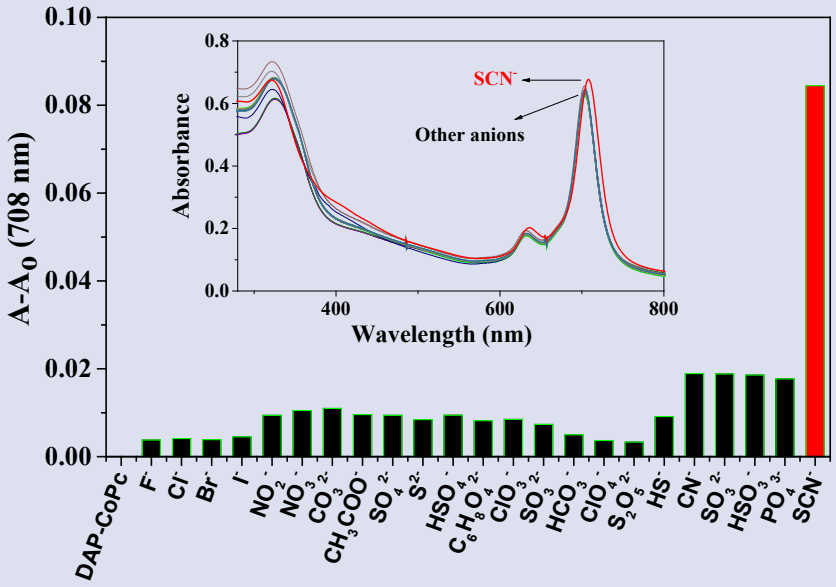


Figure 1. The bar graphs of absorbance change of DAP-CoPc (1.0×10^{-5} M in THF for UV-vis) (where A_0 and A represent initial absorption of DAP-CoPc and after addition of other anions at 708 nm, respectively), upon the addition of 50 equiv. of aqueous SCN^-, and other anions (Insets of the figure demonstrates electronic absorption spectra).

Quantitative Analysis of SCN^- Through UV-vis Titration Method

Quantitative determination of SCN^- was achieved through the UV-vis titration method. As the molar concentration of SCN^- in the DAP-CoPc solution increased, a significant red-shift was observed in the Q band of DAP-CoPc from 703 nm to 708 nm, along with a noticeable decrease in its intensity and the appearance of a new absorption band at 400 nm (Figure 2a).

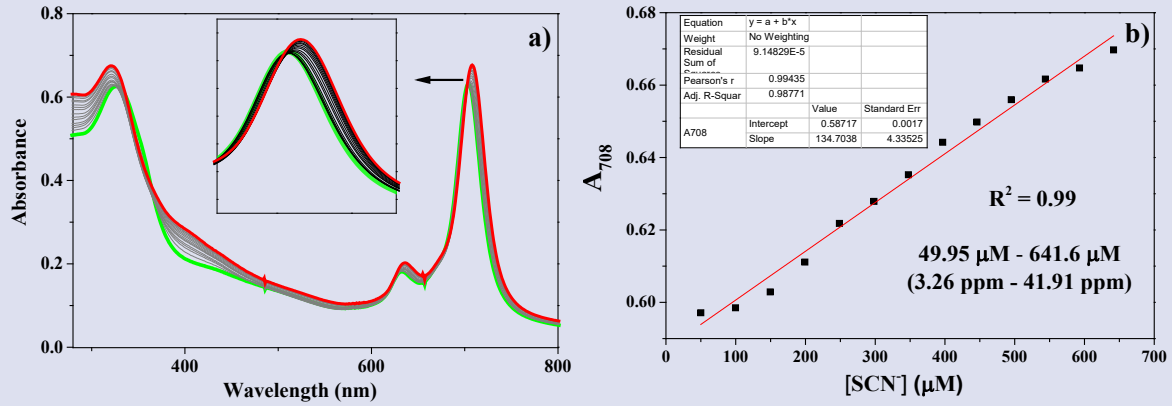


Figure 2. a) Variations in the electronic absorption spectrum and b) the resulting linear calibration curve of DAP-CoPc upon addition of aqueous SCN^-.

The UV-vis analysis enabled the quantification of SCN^-, as the absorbance at 708 nm exhibited a linear increase with rising SCN^- concentration (Figure 2b). DAP-CoPc displayed well sensing performance within the concentration range of 49.95 μM to 641.6 μM. The regression equation was determined as A708 = 134.70c + 0.59 (R2 = 0.99), where c represents the SCN^- concentration. The limit of detection, calculated using the formula 3α/slope, was found to be 11.01 μM (0.71 ppm), with α representing the standard deviation (α = 0.000495).

Response Time

A rapid response is a key advantage in sensor applications, making it a highly desirable feature. To assess this, the response times for SCN^- detection were evaluated using UV-vis method. The interaction between DAP-CoPc and SCN^- was monitored by tracking the absorbance at 708 nm in UV-vis spectroscopy, recorded at 10-second ranges following the addition of SCN^- to the DAP-CoPc solution (Figure 3). The response time was determined as the earliest point at which absorbance reached a stable state. The results demonstrated that

stabilization occurred within 100 seconds for both methods, representing a reasonable response time.

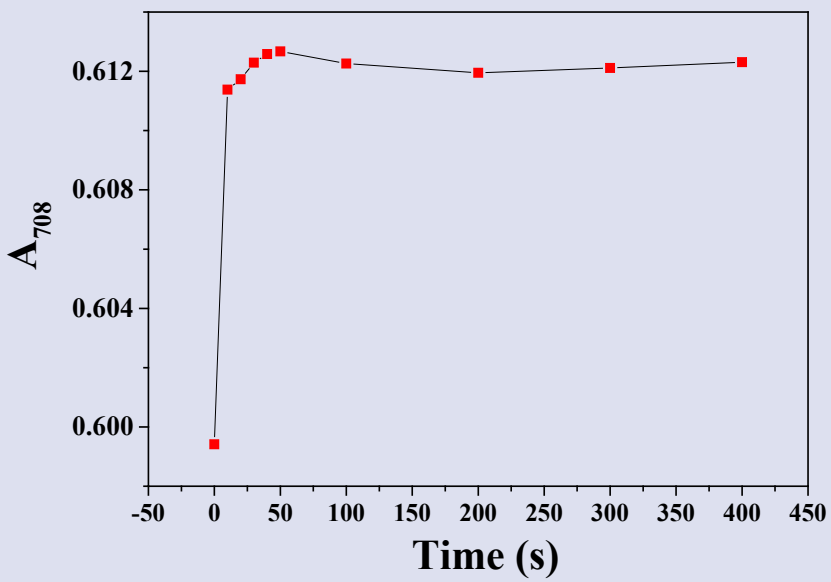


Figure 3. Response time of DAP-CoPc for UV-vis determination SCN^-.

Quantification of SCN^- in Real Samples

To evaluate the performance of the developed chemical sensor in real samples, SCN^- analysis was conducted using drinking water and lake water samples collected from the ITU. Different concentrations of SCN^--spiked real samples were added to 3 mL of DAP-CoPc (1.0 × 10-5 M) in THF within a quartz cuvette, and the UV–vis spectra were recorded. The results (Table 1) indicate that DAP-CoPc exhibits high recovery rates and low standard deviations, demonstrating its strong potential for practical application in real sample analysis.

Table 1. The SCN^- recovery outcomes and corresponding relative standard deviation (RSD) measurements in the context of real-world sample investigations encompassing drinking water and lake water samples.

Sample	Added SCN^- (µmolL-1)	Recovery (%)	RSD (n=3)
Drinking Water	49.95	100.23	0.45
	199.20	100.2	0.32
	347.60	99.72	0.97
	544.00	100.31	1.21
Lake Water	49.95	103.43	0.42
	199.20	102.24	0.71
	347.60	101.78	0.3
	544.00	101.36	0.45

Conclusion

In this study, a novel NIR phthalocyanine-based chemical sensor with notable analytical performance was synthesized for the UV-vis quantification of SCN^-. The structure of DAP-CoPc was comprehensively characterized using well-established techniques, including UV-vis, FT-IR, and MALDI-TOF. Notably, DAP-CoPc represents the first example of a phthalocyanine and porphyrin-based spectrophotometric probe specifically designed for the quantification of SCN^-.

DAP-CoPc demonstrated excellent sensor performance, achieving a remarkably low LOD of 11.01 µM for spectrophotometric (UV-vis), along with a reasonable response time of just 100 s.

Overall, the findings of this study highlight the superior sensing capabilities of DAP-CoPc in terms of selectivity, sensitivity, applicability, satisfactory response time, and durability. I strongly believe that this work marks a significant advancement in the development and application of novel NIR sensors for rapid and selective analysis of SCN^- in real samples.

Conflicts of Interest

There are no conflicts of interest in this work.

References

[1] Zhang, Y., Wang, H., & Yang, R. H., Colorimetric And Fluorescent Sensing of SCN^- Based on Meso-Tetraphenylporphyrin/Meso-Tetraphenylporphyrin Cobalt (II) System, *Sensors*, 7(3) (2007) 410-419.

[2] Wagner, A., & Ofial, A. R., Potassium Thiocyanate as Source of Cyanide for The Oxidative A-Cyanation of Tertiary Amines. *The Journal of Organic Chemistry*, 80(5) (2015) 2848-2854.

[3] Moskwa, P., Lorentzen, D., Excoffon, K. J., Zabner, J., McCray Jr, P. B., Nauseef, W. M., ... & Bánfi, B., A Novel Host Defense System of Airways is Defective in Cystic Fibrosis, *American Journal of Respiratory and Critical Care Medicine*, 175(2) (2007) 174-183.

[4] Willemin, M. E., & Lumen, A., Characterization of the Modes of Action and Dose-Response Relationship for Thiocyanate on the Thyroid Hormone Levels İn Rats Using a Computational Approach, *Toxicology and Applied Pharmacology*, 365 (2019) 84-100.

[5] Narkowicz, S., Polkowska, Ż., Marć, M., Simeonov, V., & Namieśnik, J., Determination of Thiocyanate (Biomarkers of ETS) and Other Inorganic Ions in Human Nasal Discharge Samples Using Ion Chromatography, *Ecotoxicology and Environmental Safety*, 96 (2013) 131-138.

[6] Akiyama, H., Matsuoka, H., Okuyama, T., Higashi, K., Toida, T., Komatsu, H., ... & Endou, H., The Acute Encephalopathy Induced by Intake of Sugihiratake Mushroom in The Patients With Renal Damage Might Be Associated With The İntoxication of Cyanide and Thiocyanate, *Food Safety*, 3(1) (2015) 16-29.

[7] Lobo-Júnior, E. O., LS Chagas, C., & Coltro, W. K., Determination of Inorganic Cations in Biological Fluids Using a Hybrid Capillary Electrophoresis Device Coupled With Contactless Conductivity Detection. *Journal Of Separation Science*, 41(16) (2018) 3310-3317.

[8] Li, D., Xie, F., & Zhang, J., Voltammetric Behaviors and Determination of Thiocyanate on Multiwalled Carbon Nanotubes-Cetyltrimethylammonium Bromide Modified Electrode, *Electroanalysis*, 30(10) (2018) 2413-2420.

[9] Ohshima, T., Kagaya, S., Gemmei-Ide, M., Cattrall, R. W., & Kolev, S. D., The Use of a Polymer Inclusion Membrane as a Sorbent For Online Preconcentration in The Flow Injection Determination of Thiocyanate Impurity in Ammonium Sulfate Fertilizer, *Talanta*, 129 (2014) 560-564.

[10] Ammazzini, S., Onor, M., Pagliano, E., Mester, Z., Campanella, B., Pitzalis, E., ... & D'Ulivo, A., Determination of Thiocyanate in Saliva By Headspace Gas Chromatography-Mass Spectrometry, Following a Single-Step Aqueous Derivatization With Triethyloxonium Tetrafluoroborate, *Journal of Chromatography A*, *1400* (2015) 124-130.

[11] Peng, C. F., Pan, N., Zhi-Juan, Q., Wei, X. L., & Shao, G., Colorimetric Detection of Thiocyanate Based on Inhibiting the Catalytic Activity of Cystine-Capped Core-Shell Au@Pt Nanocatalysts, *Talanta*, 175 (2017) 114-120.

[12] Umar, A. R., Hussain, K., Aslam, Z., Haq, M. A. U., Muhammad, H., & Shah, M. R., Ultra-trace level voltammetric sensor for MB in human plasma based on a carboxylic derivative of Calix resorcinarene capped silver nanoparticles, Journal of Industrial and Engineering Chemistry, 107 (2022) 81-92.

[13] Ali, R., & Saleh, S. M., Design a Friendly Nanoscale Chemical Sensor Based on Gold Nanoclusters for Detecting Thiocyanate Ions in Food Industry Applications, *Biosensors*, *14*(5) (2024) 23.

[14] Özbek, O., & Işıldak, Ö., All-solid-state poly (vinyl chloride) membrane thiocyanate–selective potentiometric electrode, *Journal of New Results in Science*, 10(2) (2021) 33-39.

[15] Arvand, M., Zanjanchi, M. A., & Heydari, L., Novel Thiocyanate-Selective Membrane Sensor Based on Crown Ether-Cetyltrimethyl Ammonium Thiocyanate İon-Pair as a Suitable Ionophore, *Sensors and Actuators B: Chemical*, *122*(1) (2007) 301-308.

[16] Xu, L., Yuan, R., Chai, Y. Q., & Fu, Y. Z., Novel Membrane Potentiometric Thiocyanate Sensor Based on Tribenzyltin (IV) Dithiocarbamate, *Electroanalysis: An International Journal Devoted to Fundamental and Practical Aspects of Electroanalysis*, *17*(11) (2005) 1003-1007.

[17] Hassan, S. S., Mohmoud, W. H., Elgazwy, A. S. S. H., & Badawy, N. M., A Novel Potentiometric Membrane Sensor Based on Aryl Palladium Complex for Selective Determination of Thiocyanate in The Saliva And Urine of Cigarette Smokers, *Electroanalysis: An International Journal Devoted to Fundamental and Practical Aspects of Electroanalysis*, *18*(21) (2006) 2070-2078.

[18] Wang, G. F., Li, M. G., Gao, Y. C., & Fang, B., Amperometric Sensor Used for Determination of Thiocyanate with a Silver Nanoparticles Modified Electrode, *Sensors*, *4*(9) (2004) 147-155.

[19] Amini, M. K., Shahrokhian, S., & Tangestaninejad, S., Thiocyanate-Selective Electrodes Based on Nickel and Iron Phthalocyanines, *Analytica Chimica Acta*, *402*(1-2) (1999) 137-143.

[20] Ozoemena, K. I., Nyokong, T., & Westbroek, P., Self-Assembled Monolayers of Cobalt And Iron Phthalocyanine Complexes on Gold Electrodes: Comparative Surface Electrochemistry and Electrocatalytic Interaction with Thiols and Thiocyanate, *Electroanalysis: An International Journal Devoted to Fundamental and Practical Aspects of Electroanalysis*, *15*(22) (2003) 1762-1770.

[21] Nemakal, M., Palanna, M., Sannegowda, L. K., & Kumar, P. S., Zinc Phthalocyanine Anchored Magnetite Particles: Efficient Platform for Sensing of Thiocyanate, *Journal of Electroanalytical Chemistry*, *895*, 2021 115385.

[22] Rastegarzadeh, S., & Moradpour, Z., A Novel Optical Sensor for Determination of Thiocyanate, *Analytical letters*, *40*(16) (2007) 2993-3001.

[23] Zhao, D., Chen, C., Lu, L., Yang, F., & Yang, X., A Dual-Mode Colorimetric and Fluorometric "Light On" Sensor for Thiocyanate Based on Fluorescent Carbon Dots and Unmodified Gold Nanoparticles, *Analyst*, *140*(24) (2015) 8157-8164.

[24] Kadish, K., Guilard, R., & Smith, K. M. (Eds.)., The Porphyrin Handbook: Applications of Phthalocyanines, Academic Press (2012).

[25] McKeown, N. B., *Phthalocyanine Materials: Synthesis, Structure and Function* (No. 6)., Cambridge university press (1998).

[26] Breloy, L., Yavuz, O., Yilmaz, I., Yagci, Y., & Versace, D. L., Design, Synthesis and Use of Phthalocyanines as a New Class of Visible-Light Photoinitiators for Free-Radical and Cationic Polymerizations, *Polymer Chemistry*, *12*(30) (2021) 4291-4316.

[27] Rezaee, E., Khan, D., Cai, S., Dong, L., Xiao, H., Silva, S. R. P., ... & Xu, Z. X. Phthalocyanine in Perovskite Solar Cells: A Review, *Materials Chemistry Frontiers*, 7(9) (2023) 1704-1736.

[28] Bonnett, R., Photosensitizers of the Porphyrin and Phthalocyanine Series for Photodynamic Therapy, *Chemical Society Reviews*, *24*(1) (1995) 19-33.

[29] Plekhanov, A. I., Basova, T. V., Parkhomenko, R. G., & Gürek, A. G., Nonlinear optical properties of lutetium and dysprosium bisphthalocyanines at 1550 nm with femto- and nanosecond pulse excitation, *Optical Materials*, *64* (2017) 13-17.

[30] Gorduk, O., Gencten, M., Gorduk, S., Sahin, M., & Sahin, Y., Electrochemical Fabrication and Supercapacitor Performances of Metallo Phthalocyanine/Functionalized-Multiwalled Carbon Nanotube/Polyaniline Modified Hybrid Electrode Materials, *Journal of Energy Storage*, *33* (2021) 102049.

[31] Breloy, L., Alcay, Y., Yilmaz, I., Breza, M., Bourgon, J., Brezová, V., ... & Versace, D. L., Dimethyl Amino Phenyl Substituted Silver Phthalocyanine as a UV-and Visible-Light Absorbing Photoinitiator: In Situ Preparation of Silver/Polymer Nanocomposites, *Polymer Chemistry*, *12*(9) (2021) 1273-1285.

[32] Yavuz, O., Sezen, M., Alcay, Y., Yildirim, M. S., Aribuga, H., Ozdemir, E., ... & Yilmaz, I., A new highly Selective, Sensitive and NIR Spectrophotometric Probe Based on A2B2-Type of Unsymmetrical Phthalocyanine for Hazardous Be^{2+} recognition, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *284*, (2023) 121484.

[33] Bayda, M., Dumoulin, F., Hug, G. L., Koput, J., Gorniak, R., & Wojcik, A., Fluorescent H-Aggregates of an Asymmetrically Substituted Mono-Amino Zn (II) Phthalocyanine, *Dalton transactions*, *46*(6) (2017) 1914-1926.

[34] Zhang, X. F., Xi, Q., & Zhao, J., Fluorescent and Triplet State Photoactive J-Type Phthalocyanine Nano Assemblies: Controlled Formation and Photosensitizing Properties, *Journal of Materials Chemistry*, *20*(32) (2010) 6726-6733.

[35] Yavuz, O., Alcay, Y., Kaya, K., Sezen, M., Kirlangic Atasen, S., Yildirim, M. S., ... & Yilmaz, I., Superior Sensor For Be^{2+} Ion Recognition via the Unprecedented Octahedral Crystal Structure of a One-Dimensional Coordination Polymer of Crown Fused Zinc Phthalocyanine, *Inorganic Chemistry*, *58*(1) (2018) 909-923.

[36] Wirojsaengthong, S., Aryuwananon, D., Aeungmaitrepirom, W., Pulpoka, B., & Tuntulani, T., A Colorimetric Paper-Based Optode Sensor for Highly Sensitive and Selective Determination of Thiocyanate in Urine Sample Using Cobalt Porphyrin Derivative, *Talanta*, *231* (2021) 122371.