e-ISSN: 2687-6698

Research Article

Turkish Journal of Analytical Chemistry

www.turkjac.org

2019

TurkJAC

Synthesis and analytical applications of thiosemicarbazide derivative

Abidin Gümrükçüoğlu[1*], Olcay Bekircan[2]

[1] Artvin Çoruh University, Faculty of Forestry, Department of Forestry Engineering, 08000 Artvin, Turkey
[2] Karadeniz Technical University, Faculty of Science, Department of Chemistry, 61080, Trabzon, Turkey

Abstract

1-(4-*tert*-Butylphenyl)-4-(4-trifluoromethylphenyl)carbonylthiosemicarbazide (OBS) was synthesized by reaction of 4-*tert*-butylbenzoic hydrazide with 4-(trifluoromethyl)phenylisothiocyanate. The influence of many metal cations on the spectroscopic properties of the synthesized compound was investigated in DMSO-H_2O (1:1) by means of emission spectrometry. The influence of a series of metal ions including Cu^{2+}, Co^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}, Pb^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, Ag^{+}, Ba^{2+}, Mo^{3+}, Se^{2+}, Ca^{2+}, Sn^{4+}, Sb^{3+}, Na^{+}, K^{+}, Li^{+}, Sc^{3+}, Sr^{2+}, As^{3+}, Be^{2+} and Mg^{2+} on the spectroscopic properties of the ligand was investigated by means of emission spectrometry. The compound was selectively complexed with Fe^{3+} among many metal ions. The complex stoichiometry and the stability constant were determined by fluorometric measurements. The ligand including thiosemicarbazide functional group (TSC) showed sensitivity for Fe^{3+} ion with a linear range between 0.5 and 5.5 mg/L. The new method was employed in the determination of iron in the sandy-soil reference material. A modified standard addition method was applied to remove the matrix effect. Detection and quantification limits were 0.07 and 0.214 mg/L, respectively. The simple and cost-effective method can be applied to soil samples.

Keywords: Thiosemicarbazides, Fe^{3+}, fluorescence measurements, complex stoichiometry

1. Introduction

Metals are important components of natural life [1]. Most of the metals are also essential for the human body. For example, the effects of iron on metabolism are still under investigation [2]. Iron has very important effects on human health. Because iron participates in many metabolic processes such as oxygen transport, deoxyribonucleic acid (DNA) synthesis, electron transport, hemoglobin production. But since iron can form free radicals, its amount in body tissues must be controlled and regulated. Otherwise, it causes many diseases, such as excessive iron loading from anemia. Because of this, the amount of iron that should be found in the body is also limited. Their deficiencies or excesses cause serious health problems. Therefore, there is always a need to develop a method for the detection and detection of metals in biological or environmental samples [3].

AAS and ICP methods for sensitive metal determination are generally expensive and time-consuming methods. Also, they require sample clean-up, preconcentration, and separation of interfering species before the analysis [4-9]. Namely, these methods are not fast and simple. Therefore, the development of alternative simple and fast methods is important to determine metal ions.

For metal determinations, fluoroionophore compounds have been used as a selective and sensitive analytical reagent. The ionophore part forms selectively a complex with target metal ion and it provides the selectivity of the method. The fluorophore part signals the complexation between metal ion and ionophore part through its fluorescence properties [10]. The high fluorescence property of the fluorophore group is desired for a highly sensitive analytical method. Therefore, the fluoroionophore comprising an appropriate ionophore and an effective fluorophore can be used to determine the target ion selectively and sensitively. From this point of view, many fluoroionophore compounds synthesized for metal determination are available in the literature [11-14].

Thiosemicarbazides (TSC) having the -CO-NH-NH-CS-NH- functional group are generally synthesized from reactions of hydrazides with isothiocyanates in different organic solvents [15]. TSC are used both as pharmacological active compound sand as starting compounds for the synthesis of diverse bioactive

Citation: A. Gümrükçüoğlu, O. Bekircan, Synthesis and analytical applications of thiosemicarbazide derivative, Turk J Anal Chem, 3(2), 2021, 59-63.

https://doi.org/10.51435/turkjac.1030232

***Author of correspondence:** gumrukcuogluabidin@artvin.edu.tr
Tel: +90 (466) 215 1000 →1044
Fax +90 (466) 215 10 34

Received: November 30, 2021
Accepted: December 17, 2021

heterocyclic compounds such as 1,2,4-triazole, 1,3,4-oxadiazole, 1,3,4-thiadiazole and thiazolinone [16-19]. They are also showed a wide range of various biological activities like antimicrobial [20], antiviral [21], anticancer [22], anti-inflammatory [23], anti-tubercular [24], topoisomerase IV and urease inhibitors [25,26]. Moreover, thiosemicarbazides can easily form metal complexes with different transition metals due to their donor groups such as nitrogen, oxygen, and sulfur [27]. Also, thiosemicarbazide has strong coordinating abilities with metal ions and is often used as the mother molecule for the design of metal-ion sensors. For this reason, there are many studies in the literature [28-29]. Recently, metal determination has been made by synthesizing nano-points from thiosemicarbazides with their exceptional optical stability and ease of functionality [30-31].

In this study, we report 2 ligands with thiosemicarbazide and semicarbazide functional groups. Fluorescence quenching of ligands against increasing metal ions was determined by spectrofluorimetric titrations in DMSO-H_2O (1/1). A simple spectrofluorimetric method was developed to determine Fe(III) from sand-soil reference material using a thiosemicarbazide compound derived from 4-tert-Butylbenzoic hydrazide and 4-(trifluoromethyl)phenyl isothiocyanate as the analytical ligand.

2. Experimental

2.1. Chemicals

Chemical reagents purchased from companies such as Sigma-Aldrich, Merck, Alfa Aesar and Acros were used without further purification. The standard solutions of cations (1000 mg/L, Merck) were used to prepare working solutions. A sandy-soil standard reference material (CRM-SA-C,) was purchased from High-Purity Standards, Inc. Dimethyl sulfoxide (DMSO) from Merck (spectrometric grade) was used as a solvent for fluorescence measurements.

2.2. Apparatus

Melting points were recorded using Thermo Scientific digital 9200 melting point apparatus. Proton-NMR and Carbon-13 NMR (APT) spectra were recorded on a Bruker Avance II 400 MHz NMR instrument using Dimethyl sulfoxide-d_6. A PTI Spectrofluorometer (QM-4/2006) was used for all fluorescence measurements.

2.3. Synthesis of 1-(4-*tert*-butylphenyl)-4-(4-trifluoromethylphenyl) carbonyl thiosemicarbazide (OBS)

4-*tert*-Butylbenzoic hydrazide (10 mmol) and 4-(trifluoromethyl)phenyl isothiocyanate (10 mmol) were refluxed in absolute ethanol for 40 min and, at the end of this period a white precipitate formed. The precipitated solid was filtered, washed with hot petroleum ether (35-60 °C), dried, and recrystallized from ethanol. Yield: %94; mp. 228-229 °C. FTIR-ATR (ν, cm^{-1}): 3301, 3220 (NH), 1641 (C=O), 1242 (C=S). ^{1}H NMR (400 MHz, DMSO-d_6) δ:3.83 (s, 3H, OCH$_3$), Ar-H: [7.06 (d, 2H, *J* = 8.0 Hz), 7.69-7.76 (m, 4H), 7.95(d, 2H, *J* = 8.0 Hz)], 9.95 and 10.01 (s, 2H, 2NH), 10.48 (NH); ^{13}C (APT) NMR (100 MHz, DMSO-d_6) δ: 55.90 (OCH$_2$), Ar-C: [113.99 (CH), 125.01, 125.44 (2CH), 126.21 (2CH), 130.35 (2CH), 143,58, 162.61], 120.77 (CF$_3$), 165.88 (C=O), 181.46 (C=S).

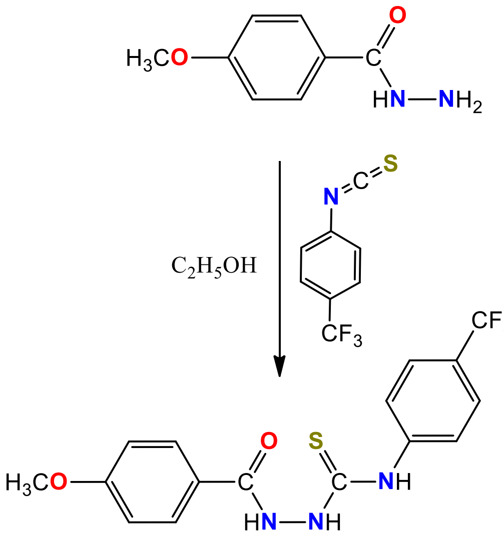
2.4. Analytical measurements

Fluorescence spectra of the ligands containing 10 M equivalents of Cu$^{2+,}$ Co^{2+}, Al$^{3+,}$ Cr^{3+}, Fe^{3+}, Pb^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, Ag^{+}, Ba^{2+}, Mo^{3+}, Se^{2+}, Ca^{2+}, Sn^{4+}, Sb^{3+}, Na^{+}, K^{+}, Li^{+}, Sc^{3+}, Sr^{2+}, As^{3+}, Be^{2+} and Mg^{2+} were recorded using 1 cm quartz cell. Different organic solvents were tested to determine the best solvent as ligand solvent. Diluted solutions of the ligands in DMSO were used in spectro fluorimetric titrations. 1-(4-*tert*-butylphenyl)4-(4-trifluoromethylphenyl)carbonylthiosemicarbazide (OBS) was 1.0 × 10^{-5} M in spectrofluorimetric measurements, and the excitation wavelength was 355 nm for this ligand. Fluorescence emission spectra were recorded in the range of 300-600 nm with the slit width of 1.0 nm. The molar-ratio method was employed to determine the stoichiometry of the complex. The stability constant of complex was calculated according to the known procedure [32]. A kind of standard addition method [33-37] was used to determine Fe^{3+} in the spiked sand-soil reference material with OBS

3. Results and discussion

3.1. Synthesis and characterization

1-(4-*tert*-butylphenyl)4-(4-trifluoromethylphenyl)-carbonylthiosemicarbazide was synthesized by reaction of 4-*tert*-butylbenzoic hydrazide with 4-(trifluoromethyl)phenyl isothiocyanate (Scheme 1). The IR spectra of the compound have C=O, C=S and N-H stretching bands of thiosemicarbazide group at 1641 cm^{-1}, 1242 cm^{-1} and 330, 3220 cm^{-1}, respectively. In the ^{1}H-NMR spectra, resonances assigned to the three N-H protons of the compound were detected at 9.95 and 10.01 ppm (s, 2H, NHCSMH) and 10.48 ppm (s, 1H, NH-C=O) respectively. In the ^{13}C-NMR spectrum, signals of C=O and C=S carbons were observed at 165.88 and 181.46 ppm.



OBS

Scheme 1. The synthesis of OBS

3.2. The effect of ions on the fluorescence spectra

The effect of 10 equivalent excess of Cu^{2+}, Co^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}, Pb^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, Ag^{+} , Ba^{2+} , Mo^{3+}, Se, Ca^{2+}, Sn^{4+}, Sb^{3+}, Na^{+}, K^{+}, Li^{+}, Sc^{3+}, Sr^{2+}, As^{3+}, Be^{2+} and Mg^{2+} ions on the fluorescence spectra of the compounds in DMSO : H_2O (1:1) was investigated. As seen from Figs. 1-4, Fe^{3+} ion cause pronounced quenching in the fluorescence spectra of QBS ligand.

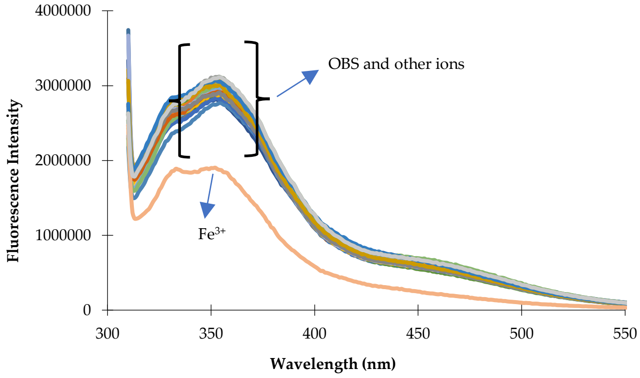


Figure 1. The effect of cations on the fluorescence spectra of OBS. OBS concentration = 1 × 10^{-5} M. Ion concentration = 1 × 10^{-4} M

Fig. 1 shows the effect of cations on fluorescence spectra of OBS compound with thiosemicarbazide functional group. OBS shows selectivity for Fe^{3+} (Fig.2). The other cations did not cause any changes in the fluorescence intensity of OBS at 355 nm (Fig.2).

For Fe^{3+} fluorimetric titrations have been performed with OBS to disclose metal-ligand interaction. Fig. 3 shows the regular fluorescence quenching with increasing Fe^{3+} concentration in the case of OBS. The change in the absorbance at 355 nm has been given in Fig. 4 inset. As seen from Fig. 4 inset, the linearity has continued until the Fe^{3+} concentration of 5.5 mg/L. A deviation from Beer's law has been observed above this concentration. The experiments have shown that this linear response can be used to determine Fe^{3+} concentration in sandy soil samples that have suitable Fe^{3+} content.

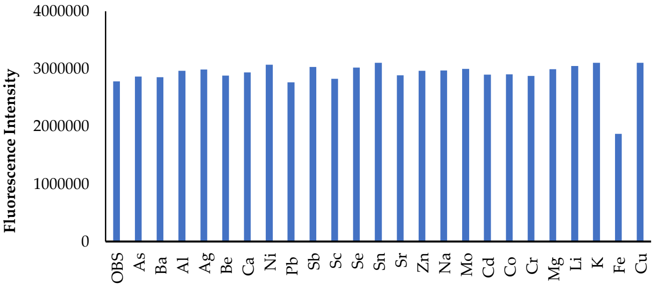


Figure 2. The effect of ions on the fluorescence spectra of OBS at 355 nm. OBS concentration = 1 × 10^{-5} M. Ion concentration = 1 × 10^{-4} M

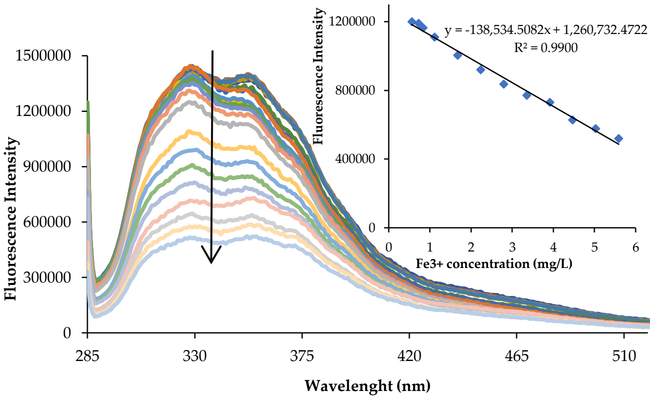


Figure 3. The quenching in the fluorescence spectra of OBS with the increasing Fe^{3+}concentration. Inset: Linear concentration range to determine Fe^{3+}. Measurements were carried out at 355 nm. OBS concentration = 1×10^{-5} M

3.3. The proposed method for Fe^{3+} determination

Acceptable recovery results were obtained with the modified standard addition method. The experimental details for the used modified standard addition method were given in the previous studies [36,37]. A constant amount of Fe^{3+} (1.0 mg/L), 2 mL of ligand (1 × 10^{-5} M), and an aliquot spiked sample (1.5 mg/L) were added to all tubes. The sample was not added to the first tube while increasing amounts of Fe^{3+} were added to the third and next tubes. The final volumes were made 2 mL with deionized water. The fluorescence intensity of all solutions was measured at 355 nm by exciting at 300 nm. The Fe^{3+} concentration was calculated from Equation 1

$$C_x=(F-F_0)/m \qquad (1)$$

where C_x is the Fe^{3+} concentration of the sample, F and F_0 are the fluorescence intensities of the first and second tubes, respectively, and m is the slope of the modified standard addition graph. The difference between F and F_0 is related to the Fe^{3+} concentration of the sample in the tubes. Fig. 4 shows the modified standard addition graph for the determination of Fe^{3+} (1.5 mg/L) in spiked sample.

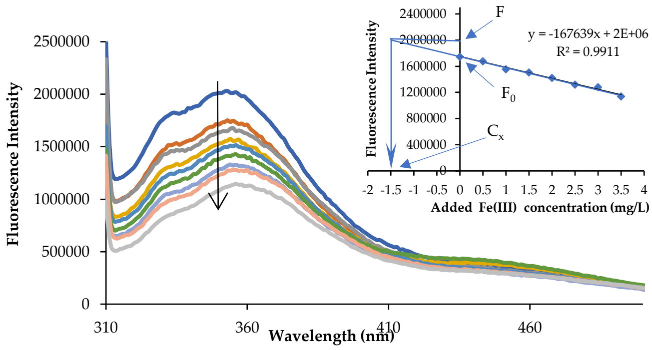


Figure 4. Changes in the fluorescence spectra of OBS over added Fe^{3+} concentration in the modified standard addition experiments. Ligand concentration = 1×10^{-5} M. Excitation at 300 nm. Measurements were carried out at 355 nm

Excitation wavelengths between 300 and 400 nm were used to obtain maximum emission intensity with OBS. The maximum fluorescence intensity was obtained when the ligand is excited with 300 nm. Excitation at 300 nm of OBS (1×10^{-5} M) gave two suitable emission bands at 333 and 355 nm in DMSO:water (1:1). Therefore, 300 nm was selected as the excitation wavelength.

The measurements were carried out in two characteristic emission wavelengths (333 and 355 nm) to determine Fe^{3+} in the spiked samples with acceptable recovery results. The recovery results were acceptable for the measurements at 355 nm. Therefore, this wavelength was selected as the measurement emission wavelength.

The optimization of constant analyte concentration is the determining stage to work the modified standard addition method according to our recent experiences [36, 37]. Also, in this study, various Fe(III) concentrations (1.0-2.0 mg/L) were tested to obtain accurate results with the modified standard addition method. The optimum constant Fe(III) concentration was found as 1.5 mg/L.

Modified standard addition experiments were carried out using the ligand solutions in the range of 5.0×10^{-5} to 1.0×10^{-6} M with increasing concentrations of Fe(III). The values of fluorescence intensity at 355 nm were plotted against Fe(III) concentration. The R^2 value of 0.9911 was obtained for a ligand concentration of 1.0×10^{-5} M (Fig.4). Therefore, in further works, this concentration was used.

A linear response of the fluorescence intensity as a function of Fe^{3+} concentration at 355 nm was observed between 0.5 mg/L and 5.5 mg/L. LOD (3xSd/m) and LOQ values (9xSd/m) were determined using the standard deviation of eleven measurements of the blank response (Sd) and the slope of the calibration line (m) according to the IUPAC recommendations.

To investigate the accuracy of the proposed method, known amount of Fe(III) were added to samples and the recovery studies were carried out. The modified standard addition method was used in the spiked samples. The % error was below 5% for concentration level (1.5 mg/L). The recovery % value was 96.01 for 1.5 mg/L Fe(III) concentration.

The intra-day and inter-day precision was estimated by analysis three independent samples spiking with 1.5 mg/L Fe(III). The precision was expressed as relative standard deviation (RSD %) and it was 7.90 for the intra-day measurements. Inter-day precision was 3.70%.

Table 1. Analytical performance data of the proposed method for Fe^{3+} determination

Excitation wavelength (nm)	300
Emission wavelength (nm)	355
Limit of detection (LOD) (mg/L)	0.07
Limit of quantification (LOQ) (mg/L)	0.214
Linear range (mg/L-mg/L)	0.5- 5.5
Constant Fe^{3+} concentration (mg/L)	1.5
Ligand concentration (mol/L)	1.0×10^{-5}
Ligand volume (mL)	2.0
Total volume (mL)	4.0
Solvent	DMSO:water (1:1)
Time before measurement (minutes)	1-2
Correlation coefficient (R^2)	0.9911

3.4. Advantages of the proposed method

Table 1 gives analytical performance data of the proposed method for Fe^{3+} determination. The proposed method can be directly applied to water samples with the Fe^{3+} concentration above 1.5 mg/L. There is no need either for the separation of Fe^{3+} ion from sandy soil sample or sample treatment such as pre concentration stage before the measurement. To remove possible matrix effects, a known modified standard addition method is employed. A time of 1-2 min was enough before measurement to obtain a stable fluorescence response. These properties make the proposed method simple and timesaving. Moreover, the method is partially environmentally friendly because the ligand is diluted with water. Spectrofluorometric methods are much cheaper compared with atomic methods. Consequently, the proposed method is timesaving, eco-friendly, simple and cheap when compared to alternative methods in the literature.

References

[1] E. Crabb, E.A. Moore, Metals and Life, 2009, UK, RSC Publishing.

[2] S. Waldvogel-Abramowski, G. Waeber, C. Gassner, A. Buser, M.M. Frey, B. Favrat, J.-D. Tissota, Physiology of iron metabolism, Transfus Med Hemoth, 41, 2014, 213-221.

[3] N. Abbaspour, R. Hurrell, R. Kelishadi, Review on iron and its importance for human health, J Res Med Sci, 19, 2014, 164-174.

[4] M.E. Mahmoud, I.M.M. Kenawy, M.M.A.H. Hafez, R.R. Lashein, Removal, preconcentration and determination of trace heavy

metal ions in water samples by AAS via chemically modified silica gel N- (1-carboxy-6-hydroxy) benzylidenepropylamine ion exchanger, Desalination, 250, 2010, 62-70.

[5] İ Narin, M. Soylak, L. Elçi, M. Doğan, Determination of tracemetal ions by AAS in natural water samples after preconcentrationof pyrocatechol violet complexes on an activated carbon column, Talanta, 52, 2000, 1041-1046.

[6] M. El Ati-Hellal, F. Hellal, M. Dachraoui, A. Hedhili, Plackett-Burman designs in the pretreatment of macroalgae for Pb, Cr and aldetermination by GF-AAS, C R Chim, 10, 2007, 839-849.

[7] M. Jamshidi, M. Ghaedi, K. Mortazavi, M. N. Biareh, M. Soylak, Determination of some metal ions by flame-AAS after their preconcentration using sodium dodecyl sulfate coated alumina modified with 2-hydroxy-(3-((1-H-indol 3-yle)phenyl) methyl) 1-H-indol (2-HIYPMI), Food Chem Toxicol, 49, 2011, 1229-1234.

[8] I. Rykowska, W. Wasiak, Chemically modified silica gel forselective solid-phase extraction and preconcentration of heavy metal ions, Int J Environ An Ch, 91, 2011, 1466-1476.

[9] B.-S. Wang, C.-P. Lee, T.-Y. Ho, Trace metal determination in natural waters by automated solid phase extraction system and ICP-MS: the influence of low level Mg and Ca, Talanta, 128, 2014, 337-344.

[10] B. Valeur, I. Leray, Design principles of fluorescent molecularsensors for cation recognition, Coordin Chem Rev, 205, 2000, 3-40.

[11] E. Gültekin, U. Kardil, Y. Topaloğlu, M. Ocak, N. Yıldırım, S. Alkan, M. Küçük, H. Bektaş, O. Bekircan, Synthesis of some new 1,2,4-triazole derivatives, investigation of their fluorescence properties and biological activities, Karadeniz Chem Sci Tech, 01, 2017, 36-42.

[12] M. Kamacı, A fluorescent film probe based on Schiff base for determination of Fe^{3+}ions, Anadolu Univ J Sci Tech A, Appl Sci Eng 18, 2017, 613-621.

[13] Y. Ji, C. Yu, S. Wen, J. Zhang, Characterization of an Al^{3+}-selective fluorescent probe based on a benzoyl hydrazine derivative and its application in cell imaging, Turk J Chem, 40, 2016, 625-630.

[14] M. Fındık, A. Uçar, H. Bingöl, E. Güler, E. Özcan, A New synthesis of ferrocene derived Schiff base sensor to determination of Zn^{2+}/Cd^{2+} ions, J Turk Chem Soc A, 2, 2015, 47-50.

[15] B. F. Abdel-Wahab, S. F. Mohamed, A. E.-G. E. Amr, M. M. Abdalla, Synthesis and reactions of thiosemicarbazides, triazoles, and Schiff bases as antihypertensive α-blocking agents, Monatsh Chem, 139, 2008, 1083-1090.

[16] S. Singhal, S. Arora, S. Agarwal, R. Sharma, N. Singhal, A review on potential biological activities of thiosemicarbazides, World J Pharm Pharm Sci, 2013, 2, 4661-4681.

[17] A.G. Galina, N.K. Angelina, Thiosemicarbazides in thesynthesis of five- and six membered heterocyclic compounds, Russ Chem Rev, 81, 2012, 494-523.

[18] A.A. Hassan, A.M. Shawky, Thiosemicarbazides in heterocyclization, J Heterocyclic Chem, 48, 2011, 495-516.

[19] S.G. Kücükgüzel, E.E. Oruc, S. Rollas, F. Sahin, A. Özbek, Synthesis, characterisation and biologicalactivity of novel 4-thiazolidinones, 1,3,4-oxadiazoles and some related compounds, Eur J Med Chem, 37, 2002, 197-206.

[20] T. Plech, M. Wujec, A. Siwek, U. Kosikowska, A. Malm, Synthesis and antimicrobial activity of thiosemicarbazides,s-triazoles and their Mannich bases bearing 3-chlorophenyl moiety, Eur J Med Chem, 46, 2011, 241-248.

[21] G. Cihan-Üstündag, E. Gürsoy, L. Naesens, N. Ulusoy-Güzeldemirci, G. Çapa, Synthesis and antiviral properties of novel indole-based thiosemicarbazides and 4-thiazolidinones, Bioorgan Med Chem, 24, 2016, 240-246.

[22] Y. Dadaş, G. P. Coşkun, O. Bingol-Akpinar, D. Ozsavci, Ş. G. Kucukguzel, Synthesis and anticancer activity of tolmetin thiosemicarbazides, Marmara Pharm J, 19, 2015, 259-267.

[23] M. Amir, S. Kumar, Synthesis and evaluation of anti-inflammatory, analgesic, ulcerogenic and lipid peroxidation properties of ibuprofen derivatives, Acta Pharmaceut, 57, 2007, 31-45.

[24] K.D. Thomas, A.V. Adhikari, S. Telkar, I.H Chowdhury, R. Mahmood, N.K Pal, G. Row, E. Sumesh, Design, synthesis and docking studies of new quinoline-3-carbohydrazide derivatives as antitubercular agents, Eur J Med Chem, 46, 2011, 5283-5292.

[25] A. Siwek, P. Staczek, J. Stefanska, Synthesis and structure-activity relationship studies of 4-arylthiosemicarbazidesas topoisomerase IV inhibitors with Gram-positive antibacterial activity. Searchfor molecular basis of antibacterial activity of thiosemicarbazides, Eur J Med Chem, 46, 2011, 5717-5726.

[26] B. Ali, K.M. Kahan, A. Kanwal, S. Hussain, S. Hussain, M. Ashraf, M. Raiz, A. Waddood, S. Perveen, Synthetic nicotinic/isonicotinic thiosemicarbazides: In vitro urease inhibitory activities and molecular docking studies, Bioorg Chem, 79, 2018, 34-45.

[27] M.K. Bharty, A. Bharti, R. Chaurasia, U.K. Chaudhari, S.K. Kushawaha, P.K. Sonkar, V. Ganesan, R.J. Butcher, Synthesis and characterization of Mn(II) complexes of 4-phenyl(phenyl-acetyl)-3-thiosemicarbazide, 4-amino-5-phenyl-1,2,4-triazole-3-thiolate, and their application towards electrochemical oxygen reduction reaction, Polyhedron, 173, 2019, 114125.

[28] W. Qingming, T. Yingzi, W. Nianhua, L. Zhixiang, W. Wenling, A multifunctional fluorescence sensor for Cd^{2+}, PO$_4^{3-}$ and Cr^{3+} in different system and the practical application, Spectrochim Acta A, 201, 2018, 216-222.

[29] A. Kumar, D. Kumar, M. Chhibbe, Determination of Mercury Ions in Aqueous Medium and Urine Sample Using Thiocarbohydrazide Based Sensor, Chemistryselect, 2020, 13738-13747.

[30] M. Mehraban, M. Manoochehri , F.A. Taromi , Trace amount determination of Cd(ii), Pb(ii) and Ni(ii) ions in agricultural and seafood samples after magnetic solid phase extraction by MIL-101(Cr)/phenylthiosemicarbazide-functionalized magnetite nanoparticle composite, New J Chem, 2018, 176361-7643.

[31] F. Zheng, H. Jiantong, J. Fengchun, W. Mengjiao, C. Fengling, Utilizing the interfacial reaction of naphthalenyl thiosemicarbazide-modified carbon dots for the ultrasensitive determination of Fe (III) ions, 225, 2020, 117485.

[32] J. Bourson, B. Valeur, Ion-responsive fluorescent compounds 2 Cation-steered intra molecular charge transfer in a crowned merocyanine, J Phys Chem, 93, 1989, 3871-3876.

[33] M. Ocak, T. Ak, A. Aktaş, N. Özbek, O.C. Çağılcı, A. Gümrükçüoğlu, H. Kantekin, Ü. Ocak, H. Alp, Metal complexation propertiesof Schiff bases containing 1,3,5-triazine derived from 2-hydroxy-1-naphthaldehyde in solution. A simple spectrofluorimetric method to determine mercury (II), J Fluoresc, 27(1), 2017, 59-68.

[34] N. Özbek, H. Alp, G. Çelik, T. Ak, O.C. Çağılcı, M. Yaylı, Ü. Ocak, M. Ocak, A simple spectrofluorimetric method for iron determination with a chalcone-based Schiff base, J Fluoresc, 27(2), 2017, 635-641.

[35] A. Başoğlu, Ü. Ocak, S. Fandaklı, N. Yaylı, A rapid and sensitive spectrofluorometric method for the determination of Au(III) based on fluorescence quenching of a 1,3,5-triphenyl-2-pyrazoline, Turk J Chem, 42, 2018, 1045-1055.

[36] A. Başoğlu, G. Tosun, M. Ocak, H. Alp, N. Yaylı, Ü. Ocak, Simple time-saving method for iron determination based on fluorescence quenching of an azaflavanon-3-ol compound, J Agr Food Chem, 63, 2015, 2654-2659.

[37] Y. Çağlar, E.T. Saka, H. Alp, H. Kantekin, Ü. Ocak, M. Ocak, A simple spectrofluorimetric method based on quenching of a nickel(II)-phthalocyanine complex to determine iron (III), J Fluoresc, 26, 2016, 1381-1389.

Supplementary materials

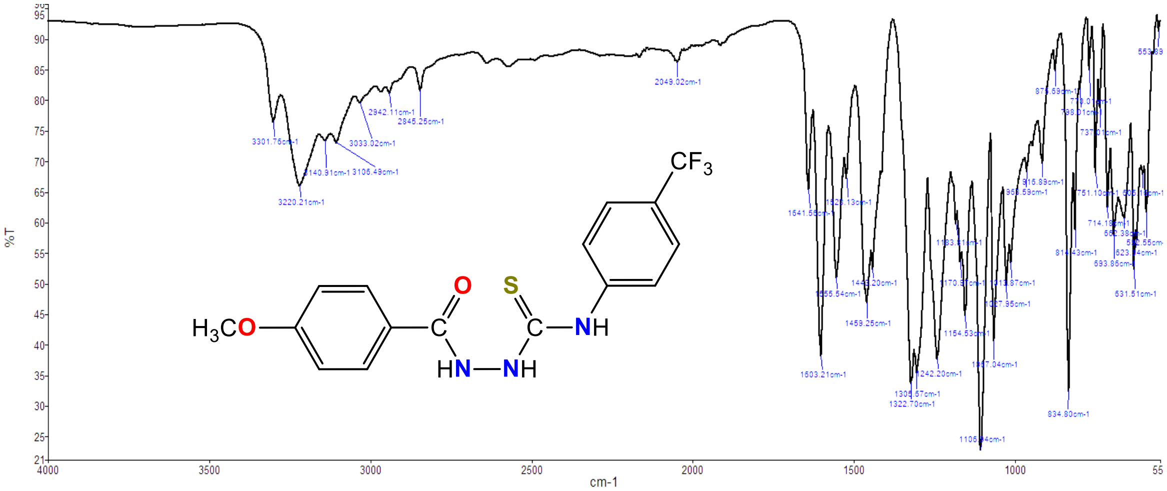


Figure 1. IR spectrum of OBS.

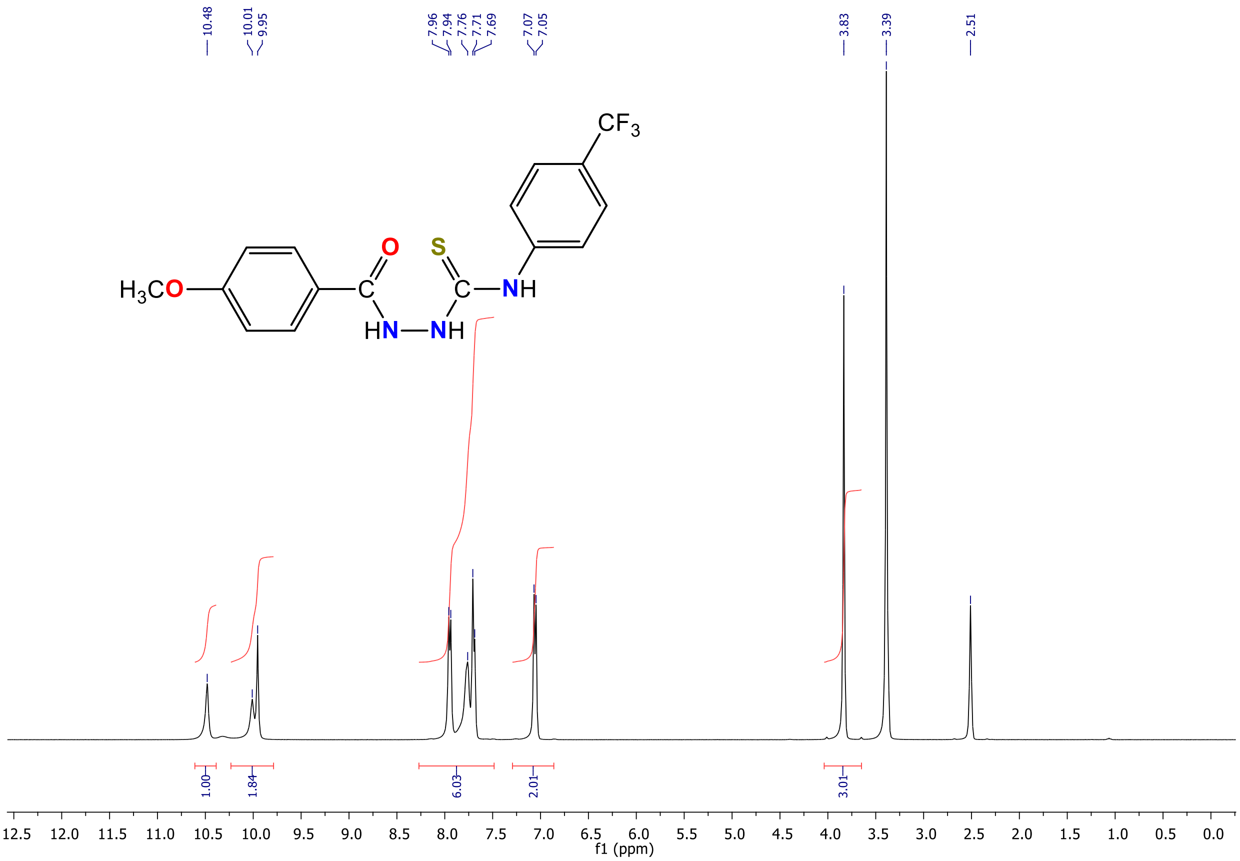


Figure 2. ^{1}H NMR spectrum of OBS.

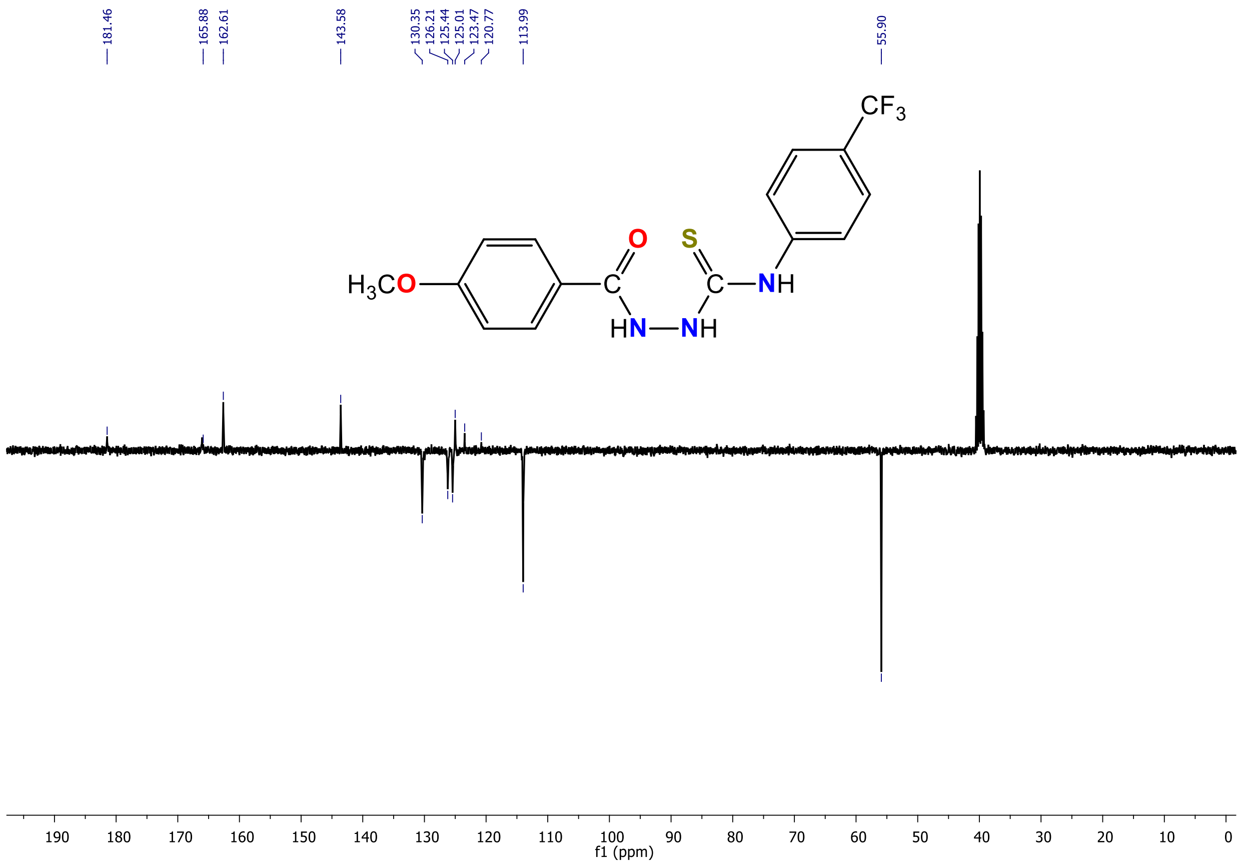


Figure 3. ^{13}C NMR spectrum of OBS.