Journal of Elementology ISSN 1644-2296

Wierzbicka E. 2020.
Novel methods of nitrate and nitrite determination – A review.
J. Elem., 25(1): 97-106. DOI: 10.5601/jelem.2019.24.3.1848

RECEIVED: 16 April 2019
ACCEPTED: 21 August 2019

REVIEW PAPER

NOVEL METHODS OF NITRATE AND NITRITE DETERMINATION – A REVIEW*

Elwira Wierzbicka

Department of Chemistry
University of Warmia and Mazury in Olsztyn, Poland

Abstract

Nitrates and nitrites are common in water systems, sewage and food. Their presence in low amounts in aquatic ecosystems is desirable for the growth and development of living organisms. At concentrations exceeding safe levels, these compounds pose a wide variety of health risks. Due to their highly toxic effect on the environment and living organisms, it is necessary to determine and monitor their levels in water, sewage and food. This paper is a review of conventional and modern methods of detection and determination of nitrates in water and sewage, including ones based on colorimetry, spectrophotometry and chromatography. The conventional methods, although offering an array of advantages, present certain disadvantages, such as considerable time consumption, susceptibility to ionic interference and sometimes requiring expensive equipment. Among the analysed methods, an innovative method based on electrochemical sensors using nanomaterials deserves attention. The recent application of nanomaterials such as carbon nanotubes (CNT), metal nanoparticles, nanocomposites or nanoclasters has attracted much interest in the field of developing electrochemical sensors for nitrate and nitrite detection. Owing to the selectivity, repeatability, simplicity, rapid response, sensitivity and ease of operation, nanoelectrodes may be used for routine monitoring of the environment. Nitrate determination using electrochemical sensors constitutes an excellent alternative to all other available analytical methods.

Keywords: nitrate, nitrite, spectrophotometric, elctrochemical detection, determination, nanoparticle electrode, review.

Elwira Wierzbicka, Ph.D., Department of Chemistry, University of Warmia and Mazury in Olsztyn, pl. Łódzki 4, 10-957 Olsztyn, phone: +48(89)5234247, e-mail: elwiraw@uwm.edu.pl.
* This work was supported by grant no 20.610001-110.

INTRODUCTION

Nitrates occurring in low amounts in aquatic systems ensure the development of aquatic vegetation and organisms. Excessive accumulation of nitrates (next to phosphates), above the safe limits of nutrients in aquatic ecosystems, results in an uncontrolled growth of vegetation conducive to eutrophication. Subsequently, oxygen reserves are depleted, aquatic organisms die and the aquatic environment undergoes irreversible changes. Nitrates, widely used in mineral fertilisers and food preservatives, commonly enter water, soils and wastewater. They are leached from the soil, hence they can pollute groundwater and surface water bodies.

According to the WHO recommendations, it is assumed that the maximum admissible nitrate level in potable water should not exceed 44 mg kg^{-1}. The European Union regulations determine the maximum safe level of nitrites in potable water at 0.1 mg kg^{-1} (Chen et al. 2007). It is believed that a nitrate content in the human body above this level causes serious health problems, especially of the alimentary system. At low pH, these compounds can react with secondary and tertiary amines, giving rise to the formation of carcinogenic compounds, such as N-nitrocompounds (Özdestan, Üren 2010, Bryan et al. 2012). It has been indicated that methaemoglobinaemia, i.e. *baby blue syndrome,* which is a threat especially to small children, is caused by excessive nitrate levels in diets (Gladwin et al. 2009, Cassidy, Duggan 2015). Nitrates have the capacity to oxidise haemoglobin to methaemoglobin irreversibly, which hinders the oxygen transport mechanism, leading to death. These compounds are regarded as probable factors of high risk of kidney diseases (Mirmiran et al. 2016). The control of nitrate levels in water and food products is becoming a priority issue, and the determination of nitrate in samples is therefore essential.

The scientific literature offers a wide selection of review papers on nitrate and nitrite detection and determination techniques (Moorcroft et al. 2001, Wang et al. 2017, Asharat, Mukho-Padhyay et al. 2018). This paper presents selected methods which in the recent years have been developed substantially owing to the application of modern materials, compilation of several analytical techniques or desing of novel solutions. Determination of nitrates using a wide variety of analytical techniques is crucial for the monitoring of environment. There are numerous available nitrogen determination methods, including spectrophotometry (Miranda 2001), chemiluminescent (He et al. 2007), spectrofluorimetric (Huang et al. 2000), chromatography (Campanella et al. 2017), electrochemical analysis (Liangyun Yu et al. 2015) and flow injection methods (Baomin Liu et al. 2016).

SPECTROPHOTOMETRIC METHODS

Spectrophotometric methods, most frequently based on the Griess method, are widely used in the determination of nitrates and nitrites. The Griess reaction, first described in 1879, was initially used to identify nitrites in saliva, and this technique served throughout the following century for nitrite identification in biological fluids. To determine nitrates, prior to the diazotation reaction, chemical or enzymatic reduction of nitrates to nitrites is performed. The two-phase process involves diazotation, where nitrites react with sulphanilamide, and then conjugation, where the diazotation product in an acidic medium reacts with amines, e.g. with *N*-(1-naphthyl) ethylenediamine (NED). to produce pink azo dye (λ=540 nm). Nitroaniline and *p*-aminoacetofenon were also used in the diazotation reaction, while 1-naphtol, 1-amino-naphtalen,1-naphtolo-4-sulphonian,1,3-diaminobenzene were also utilised in the conjugation reaction. The key phase in nitrate determination is the reduction to nitrites, which is catalysed by cadmium and copper (Wang 1998), hydrazine with copper catalyser, zinc column (Elis et al. 2011, Merino et al. 2000), titanium or VCl_3 (Miranda 2001, Woollard, Indyk 2014, Lin et al. 2016). Biological reduction, which does not produce toxic waste, is sometimes used. Enzymatic biocatalysers employed in the colorimetric reaction include NaR enzymes or NaR-containing microorganisms (Jobgen et al. 2007, Wittbrodt et al. 2015).

Spectrophotometric detection using the Griess reaction, which is a relatively simple method of nitrate and nitrite determination, has a range of sensitivity from 0.02 to 2 M. The colorimetric method allows separate determination of all nitrates or nitrates and nitrites. Although this method is simple and offers relatively low detection limits, it has some drawbacks, e.g. interference of some organic substances and some ions, and masking agents such as EDTA (Narayana, Sunil 2009) or trisodium citrate. Although it is frequently and willingly used because of the simplicity of measurements and low analytical costs, this method does not ensure sufficient sensitivity since nitrates are detected at a micromolar level. Complex analytical methods are used to solve such problems, improve precision and decrease the nitrate and nitrite detection limits Croitoru (2012) developed a HPLC/ /VIS method for the simultaneous detection of nitrates and nitrites in biological samples in the detection range of ppb for nitrites and hundredths of ppb for nitrates. Nitrates are determined by pre-column derivatisation using the Griess reaction. Kunduru et al. (2017) produced film from synthesised polymers with side chains from phosphoric acid and zinc. These compounds emulate the Griess reagents. The film was used to detect nitrates in ammonium nitrate and sodium nitrate at a detection limit of 4 ppm. Ibrahim et al. (2019) proposed a simple and effective method of colorimetric detection using the reaction of conjugation of diazo *p*-aminobenzoic acid (PABA) and fluoroglucynol in an acidic medium, where yellow azo dye waso btained, with an anticipated maximum absorption of 434 nm. The colorimetric sensor may

be used to detect nitrites in water samples in a detection range from 0.05 to 1 mg kg^{-1}.

In 2010, Hernandez et al., using a spectrophotometric flow injection analysis based on a modified Griess-Ilsovay reaction, developed an individual and combined assay. The modification of the conventional method enables an analysis of approx. 40 samples/h with a detection range from 22-44 μg. Owing to its simplicity, cost effectiveness, precision and rapidness, this method may be used for monitoring the environment. The application of a spectrophotometric automatic flow injection analysis (FIA) with VCl_3 as a Griess reaction reducer (instead of toxic cadmium) in the determination of nitrates and biological samples improves the sensitivity and reduces the assay time-consumption significantly (Lin et al. 2016). The detection range and the detection limit of this method are from 0-100 μM and 0.1 μM, respectively. The throughput reaches 20 samples/h. An automatic flow method in a loop according to the Griess reaction (Baomin Liu et al. 2016) was applied to determine nitrates in water samples. The detection limit of this method was 0.02 μM and the assay time was short: ~4 min/sample. Li et al. (2018) developed an innovative sensor using the Griess reaction modulation and a strategy of conducting three analyses (colorimetric, fluorescence and SERS) for quick determination of nitrites in a complex sample matrix.

ELECTROCHEMICAL METHODS

In the recent years, a wide range of review papers has been published on nitrate and nitrite electrochemical detection methods (Wang et al. 2017, Eshrat et al. 2018). Various methods and analytical techniques have been presented, among which the voltamperometric method seems to have drawn the most interest. This method has been particularly extensively developed, and huge progress has been made in the application of innovative materials and solutions. Traditional unprotected electrode materials (copper, nickel, platinum, cadmium, gold, glassy carbon) used previosuly caused problems connected with their passivation and toxicity (Wang et al. 2017). Attempts have been made to solve such obstacles by modifying an electrode's surface with organic and inorganic catalysers and enzymes. This involves electrolytical improvement of the surface of electrodes in order to obtain highly specific catalytic activity for redox reactions. The formation of a developed and active electrode's surface enhances the electron transfer kinetics, and improves the sensitivity and response signal of the electrode.

In recent years, nanomaterials have attracted much interest. Nanoelectrodes have found a perfect application in electrochemical detection. When applied to modify the surfaces, they improve the electrocatalytical capability of electrodes as reducing agents. Nanoparticles with their small size and large surface constitute perfect electrocatalysers. Apart from nanoparticles, nanodots, nanotubes, nanoshells, nanoclusters, nanofibers and nanocompos-

ites have also been applied in electrochemical sensors (Haldorai et al. 2016, Li et al. 2017). Recent studies have reported the use of bovine serum albumin-coated gold-nanoparticles BSA-AuNP (Shankar 2018), magnetic nanoparticles – MNP – and magnetic nanocomposite NP-SiO_2 (Ispas 2018) as modifiers in electrochemical sensors, employed so as to improve the sensitivity and precision of nitrate determination. A silver nanotube (Ag/HNT/MoS_2)-modified carbon paste electrode – CPE (Ghanei-Motlagh, Taher 2018) was used in a nitrite determination assay. A nanoclaster-coated (Ag/Cu/MWNT) graphene composite electrode (GCE) resulted in its high electrocatalytic nitrite oxidation activity (Yi Zhang 2018). Nitrogen-doped graphene quantum dots modified with nitrogen-doped carbon nanofiber composite (NGQDs@ NCNF) provided a large area of the active surface to be used in effective nitrite detection (Li et al. 2017). Nanotubes (Kuralay et al. 2015, Bagheri et al. 2017) and nanocomposites (Rajalakshmi, John 2015, Boussema et al. 2016, Zhang et al. 2016) applied on the nanoelectrode surface successfully improved analytical performance. Nanocomposite electrocatalytic capability depends on the material used. Nanocomposites obtained through the combination of varied nanomaterials offer much higher sensitivities and improved selectivity. Table 1 presents selected nanoelectrodes with limits of detection and detection ranges.

The exceptional properties of nanoelectrodes offer low detection levels of μM or even nM as well as wide detection ranges. The study results indicate that the application of nanomaterials has become a promising alternative in electrode modification. Nanoelectrodes have shown great potential in the analysis of a wide range of environmental samples. Electrochemical methods of nitrite detection offer high selectivity and sensitivity, and they are quick and cost-effective when compared with the traditional methods (Yi Zhanga et al. 2018).

STATISTICAL METHODS

In view of the lack of or/and accessibility to an online nitrogen compound measurement system (especially in wastewater), research into virtual (soft) sensors is emerging. Virtual sensors utilise easily available parameters such as pH, conductivity and particles which are measured in real-time and combine historical data and advanced statistical analysis. Algorithms to estimate nitrogen compounds are then produced. Wang et al. (2019) presented a concept of COD and total P prediction using virtual sensors, which can be used analogously for the prediction of nitrogen compounds. Mulas et al. (2012) presented an example of estimating nitrates during denitrification in wastewater.

Table 1

Characteristics of various nanoelectrodes.

Electrode	Nitrate/nitrite	Detection limit	Detection range	References
Cu / MWCNT / RGO / GCE	both	30 nM and 20 nM	0.1 to 75 μM	Bagheri et al. (2017)
Ag-PAMAM	nitrite	0,4 μM	4.0 μM to 1,44 mM	Danlei Ning et al. (2014)
TOSC-MoS_2/ GCE	nitrite	2.0 mM	6.0- 3140 and 3140-4200 mM	Wang et al. (2017)
EAG / SPCE	nitrite	38 nM	0.1 mM to 16.4 mM	Palanisamy et al. (2014)
Cu_2O/CNT	nitrite	0.018 nM	0.1 nM to 1 mM	Lei Wu et al. (2018)
Ag/Cu/MWNTs/GCE	nitrite	2 × 10 - 7 mol L^{-1}	1.0 mol L^{-1} to 1.0 $mmol^{-1}$	Yi Zhang et al. (2018)
AgPs	nitrite	3 μmol L^{-1}	0.05 to 1.0 mmol L^{-1}	Menart et al. (2015)
Cu@Pt/Gr	nitrite	15.64 nM	1 μM 1mM and 1-15 mM	Abdel Hameed et al. (2018)
ERGO-Pd	nitrite	0.095 mM	0.04 and 108 μM	Ya Zhang et al. (2013)
AgNPs/MWCNTs/GCE	nitrite	2 to 425 μM	1 mM-100 mM	Yue Wan et al. (2017)
Ag/HNT/MoS_2	nitrite	15.64 nM	0.7 μM	Ghanei-Motlagh, Taher (2018)

CONCLUSION

The content of nitrites and nitrates is one of the basic parameters in the monitoring of surface water and groundwater. Recent progress in new technologies has enhanced the capacity of identification and determination of nitrates and nitrites. In recent years, many publications have appeared that focus on the application of nanomaterials in the construction of electrochemical sensors. Novel sensors based on nanoparticles offer enhanced electrochemical properties in the detection of nitrates and nitrites owing to their specific surface area and high electric conductivity. When compared with the conventional methods, which usually require time-consuming analysis and costly instruments, with this technology nitrates can be determined directly in a sample.

REFERENCES

Abdel Hameed R.M., Shymaa S. Medany. 2018. *Sensitive nitrite detection at core-shell structured Cu@Pt nanoparticles supported on graphene*. App. Surf. Sci., 458: 252-263.

Abid Z., Cross A. J., Sinha R. 2014. *Meat, dairy and cancer,* Am. J. Clin. Nutr., 100(1): 386-393.

Baciua A., Maneaa F., Popa A., Podea R., Schoonmanb J. 2017, *Simultaneous voltammetric detection of ammonium and nitrite from groundwater at a silver-electrodecorated carbon nanotube electrode*. Proc. Saf. Environ., 108: 18-25.

Bagheri H., Hajian A., Rezaei M., Shirzadmehr A. 2017. *Composite of Cu metal nanoparticles--multiwall carbon nanotubes-reduced graphene oxide as a novel and high performance platform of the electrochemical sensor for simultaneous determination of nitrite and nitrate.* J. Hazard. Mater., Part B, 324: 762-772

Baomin L., Haitao S., Shu W., Zhen Z., Ying L., Dongxing Y., Jian M. 2016 *Chemical automated determination of nitrite in aqueous samples with an improved integrated flow loop analyzer*. Sensor Actuat B-Chem, 237: 710-714.

Boussema F., Haddad R., Ghandour Y., Belkhiria M.S., Cosnier S. 2016. *Polyoxometalate [PMo11O39]7−/carbon nanocomposites for sensitive amperometric detection of nitrite.* Electrochimica Acta, 222: 402-408.

Bryan N.S., Alexander D.D., Coughlin J.R., Milkowski A.L., Boffetta P. 2012. *Ingested nitrate and nitrite and stomach cancer risk: An updated review*. Food Chem. Toxicol., 50: 3646-3665. DOI: 10.1016/j.fct.2012.07.062

Butler A. 2015. *Nitrites and nitrates in the human diet: Carcinogens or beneficial hypotensive agents?* J. Ethnopharmacol., 167: 105-107.

Campanella B., Onor M., Pagliano E., 2017. *Rapid determination of nitrate in vegetables by gas chromatography mass spectrometry*. Anal. Chim. Acta, 980: 33-40. https://doi.org/10.1016/j.aca.2017.04.053

Cassidy N., Duggan E. 2015. *Potential pitfalls with the treatment of acquired methemoglobinemia*. Irish Med. J., 108: 27-28.

Chen H., Mousty C., Cosnier S., Silveira C., Moura J.J.G., Almeida M.G. 2007. *Highly sensitive nitrite biosensor based on the electrical wiring of nitrite reductase by [ZnCr-AQS] LDH.* Electrochem. Commun., 9: 2240-2245.

Croitoru M.D. 2012. *Nitrite and nitrate can be accurately measured in samples of vegetal and animal origin using an HPLC-UV/VIS technique*. J. Chromatogr., 911: 154-161.

Dan Li, Yadan Ma, Huazhen Duan, Wei Deng, Dawei Li 2017. *Griess reaction-based paper strip for colorimetric / fluorescent / SERS triple sensing of nitrite*. Biosens. Bioelectron., 99: 389-398.

Danlei Ning, Hongfang Zhang, Jianbin Zheng. 2013. *Electrochemical sensor for sensitive determination of nitrite based on the PAMAM dendrimer-stabilized silver nanoparticles*. J. Electroanal. Chem., 717-718.

Ellis P.S., ShabaniA. M.H., Gentle B.S., McKelvie I.D. 2011. *Field measurement of nitrate in marine and estuarine waters with a flow analysis system utilizing on-line zinc reduction*. Talanta, 84: 98-103.

Eshrat E.M., Alahi Subhas Chandra Mukho-padhyay S.H. 2018. *Detection methods of nitrate in water: A review*. Sensor Actuat. A-Physical., 280: 210-221. https://doi.org/10.1016/j.sna.2018.07.026

Ghanei-Motlagh M., Taher M.A. 2018. *A novel electrochemical sensor based on silver/halloysite nanotube/ molybdenum disulfide nanocomposite for efficient nitrite sensing*. Biosens. Bioelectron., 109: 279-285

Gladwin M.T, Grubina R., Doyle M.P. 2009. *The new chemical biology of nitrite reactions with hemoglobin: R-state catalysis, oxidative denitrosylation and nitrite reductase/anhydrase*, Acc. Chem. Res., 42: 157-167.

Haldorai Y, Hwang S.K., Gopalan A.I., Huh Y.S., Han Y.K., Voit W., Sai-Anand G., Lee K.P. 2016. *Direct electrochemistry of cytochrome c immobilized on titanium nitride/multi-walled carbon nanotube composite for amperometric nitrite biosensor*. Biosens. Bioelectron., 79: 543-552.

He D., Zhang Z., Huang Y., Hu Y. 2007. *Chemiluminescence microflow injection analysis system on a chip for determination of nitrite in food*. Food Chem, 101: 67-672.

Honggui Wang, Fangfang Wen, Yajie Chen, Ting Sun, Yao Meng, Ya Zhang. 2016. *Electrocatalytic determination of nitrite based on straw cellulose/ molybdenumsulfide nanocomposite*. Biosens. Bioelectron., 85: 692-697.

Huang Z., Korenaga T., Helaleh M.I. 2000. *Kinetic spectrofluorimetric determination of nitrite in water samples and nitrogen dioxide in the atmosphere sampled by the liquid droplet method*. Microchim. Acta, 134: 179-183.

Ibrahim M.H., Mahgoub Z.X., Hassan I.S, Abdu I., Xiong L., Shan D., Lu X. 2019. *A simple yet sensitive colorimetric nitrite ions assay based on diazotization with pAminobenzoic and coupling with phloroglucinol in acidic medium*. Spectrochim. Acta A, 210: 398-404.

Ispas G.M., Craciunescu I., Porav S., Turcu R., Gligor D. 2018. *New type of electrode material based on magnetic nanoparticles with high potential applicability in electrochemical sensors for nitrite detection*. Sensor Actuat. A-Phys, 276: 43-51.

Jobgen W.S., Jobgen S.C., Li H., Meininger C.J., Wu G. 2007. *Analysis of nitrite and nitrate in biological samples using high-performance liquid chromatography*. J. Chromatogr. B, 851: 71-82.

Kunduru K.R., Basu A., Tsah T., Domb A.J. 2017. *Polymer with pendant diazo-coupling functionality for colorimetric detection of nitrates*. Sensor Actuat. B-Chem, 251: 21-26.

Kuralay F., Dumangöz M., Tun S. 2015. *Polymer/carbon nanotubes coated graphite surfaces for highly sensitive nitrite detection*. Talanta, 144: 1133-1138.

Lei Wu, Xiaojing Zhang, Minghua Wang, Linghao He, Zhihong Zhang J. 2018. *Preparation of Cu2O/CNTs composite and its application as a sensing platform for detecting nitrite in water environment,* Measurement, 128: 189-196.

Li L., Liu D., Wang K., Mao H., You T. 2017. *Quantitative detection of nitrite with N- doped graphene quantum dots decorated N-doped carbon nanofibers composite-based electrochemical sensor*. Sensor Actuat. B-Chem., 252: 17-23.

Liangyun Yu, Qi Zhang, Qin Xu, Dangqin Jin, GendiJin, Kexin Li, Xiaoya Hu. 2015. *Electrochemical detection of nitrate in $PM_{2.5}$with a copper-modified carbon fiber micro-disk electrode*. Talanta, 143: 245-253. https://doi.org/10.1016/j.talanta.2015.04.049

Libo Li, Dong Liu, Kun Wang, Hanping Mao, Tianyan You. 2017. *Quantitative detection of nitrite with N-doped graphene quantum dots decorated N-doped carbon nanofibers composite--based electrochemical sensor*. Sensor Actuat. B-Chem., 252: 17-23.

López Pasquali C.E., Gallego-Picó A., Fernández Hernando P., Velasco M., Durand Alegría J.S. 2010. *Two rapid and sensitive automated methods for the determination of nitrite and nitrate in soil samples*. MicrochemHYPERLINK "https://www-1sciencedirect-1com--11c059865a024.han.uwm.edu.pl/science/journal/0026265X" HYPERLINK "https://www-1sciencedirect-1com-11c059865a024.han.uwm.edu.pl/science/journal/0026265X"J, 79-82.

Menart E., Jovanovski V., Hočevar S.B. 2015. *Silver particle-decorated carbon paste electrode based on ionic liquid for improved determination of nitrite*. Electrochem. Com., 52: 45-48. https://doi.org/10.1016/j.elecom.2015.01.017

Merino L., U. Edberg, G. Fuchs, P. Aman. 2000. *Liquid chromatographic determination of residual nitrite/nitrate in foods: NMKL collaborative study*. J. *AOAC* Int., 83: 365-375.

Mirmiran P., Bahadoran Z., Golzarand M., Asghari G., Azizi F. 2016. *Consumption of nitrate containing vegetables and the risk of chronic kidney disease: Tehran Lipid and Glucose Study*. Taylor & Francis, 38(6): 937-944.

Mulas M., Corona F., Haimi H., Sundell L., Heinonen M., Vahala R. 2012. *Nitrate estimation in the denitrifying post-filtration unit of a municipal wastewater treatment plant: the Viikinmäki case*. Water Sci Technol., 65(8): 1521-1529. DOI: 10.2166/wst.2012.038

Narayana B., Sunil K. 2009. *Spectrophotometric method of determination of nitrites and nitrates*. Eurasian J. Anal. Chem., 4: 204-214.

Özdestan O., Üren A. 2010. *Development of a cost-effective method for nitrate and nitrite determination in leafy plants and nitrate and nitrite contents of some green leafy vegetables grown in the Aegean region of Turkey*. J. Agr. Food Chem., 58(9): 5235-5240.

Palanisamy S., Karuppiah C., Chen S.M., Periakaruppan P. 2014. *Highly sensitive and selective amperometric nitrite sensor based on electrochemically activated graphite modified screen printed carbon electrode*. J. Electroanal. Chem., 727: 34-38.

Qiu-Hua Wang, Li-Ju Yu, Yang Liu, Lan Lin, Ri-gang Lu, Jian-ping Zhu, Lan He, Zhong-LinLu. 2017. *Methods for the detection and determination of nitrite and nitrate: A review*. Talanta, 165: 709-720. https://doi.org/10.1016/j.talanta.2016.12.044

Rahmati , Samani A.N. , Mahmoodi N., Mahdavi M. 2015. *Assessment of the contribution of N-fertilizers to nitrate pollution of groundwater in Western Iran*. Water Qual. Expo. Health, 7(2): 143-151.

Rajalakshmi K., John A.K. 2015. *Highly sensitive determination of nitrite using FMWCNTs-conducting polymer composite modified electrode*. Sensor Actuat. B-Chem., 215: 119-124.

Sai Zhang, Boqiang Li, Qinglin Sheng, Jianbin Zheng. 2016. *Electrochemical sensor for sensitive determination of nitrite based on the CuS–MWCNT nanocomposites*. J. Electroanal Chem., 769: 118-123

Shankar S., Gowthaman N.S.K., Abraham S. 2018. *Synthesis of albumin capped gold nanoparticles and their direct attachment on glassy carbon electrode for the determination of nitrite ion*. J. Electroanal Chem., 828: 33-40.

Shu Wang Kunning Lin, Nengwang Chen, Dongxing Yuan, Jian Ma. 2016. *Automated determination of nitrate plus nitrite in aqueous samples with flow injection analysis using vanadium (III) chloride as reductant*. Talanta, 146: 744-748.

Wang Q.H., Yu L.J., Liu Y., Lin L., Lu R.G., Zhu J.P., He L., Lu Z.L. 2017. *Methods for the detection and determination of nitrite and nitrate: A review*. Talanta, 165: 709-720.

Wang, X., Kvaal, K., Ratnaweera, H. 2019. *Explicit and interpretable nonlinear soft sensor models for influent surveillance at a full-scale wastewater treatment plant*. J. Process Contr., 77: 1-6.

Wittbrodt B.T., Squires D.A., Walbeck J., Campbell E., Campbell W.H., Pearce J.M.. 2015.

Open-source photometric system for enzymatic nitrate quantification. PLoS One, 10(8). https://doi.org/10.1371/journal.pone.0134989

Woollard D.C., Indyk H.E. 2014. *Colorimetric determination of nitrate and nitrite in milk and milk powders – Use of vanadium (III) reduction.* Int. Diary J., 35(1): 88-94.

Xu G., Song P., Reed P.I. 1992. *The relationship between gastrin mucosal changes and nitrate intake via drinking water in a high-risk population for gastric cancer in Moping County, China.* Eur J Cancer Prev., 1437-444.

Ya Zhang, Yanhua Zhao, Saisai Yuan, Honggui Wanga, Chenda Hea. 2013. *Electrocatalysis and detection of nitrite on a reduced graphene/Pd nanocomposite modified glassy carbon electrode*, Sensor Actuat. B-Chem., 185: 602-607.

Yi Zhang, Jutao Nie, Hanyu Wei, Hengtao Xu, Xinyue Wu. 2018. *Electrochemical detection of nitrite ions using Ag/Cu/MWNT nanoclusters electrodeposited on a glassy carbon electrode.* Sensor Actuat. B-Chem., 258: 1107-1116.

Yi Zhanga, Jutao Niea, Hanyu Weia, Hengtao Xub, Qi Wanga, Yanqing Conga, Jiaqi Taoa, Yi Zhanga, Linglong Chua, Yue Zhoua, 2018. *Electrochemical detection of nitrite ions using Ag/Cu/MWNTnanoclusters electrodeposited on a glassy carbon electrode.* Sensor Actuat. B-Chem., 258: 1107-1116.

Yue Wan, Yi Fan Zheng, Hua Tao Wanc, Hao Yong Yin, Xu Chun Song. 2017. *A novel electrochemical sensor based on Ag nanoparticle decorated multi-walled carbon nanotubes for applied determination of nitrites.* Food Control, 73: 1507-1513.

Yilong Z., Dean Z., Daoliang L. 2015. *Electrochemical and Other Methods for Detection and Determination of Dissolved Nitrite: A Review.* Int. J. Electrochem. Sci., 10: 1144-1168.