NITRATE ION-SELECTVE ELECTRODES – NEW CONSTRUCTIONS AND APPLICATIONS IN THE MONITORING OF NITRATE IONS IN ENVIRONMENTAL SAMPLES

C. Wardak, K. Pietrzak

Department of Analytical Chemistry, Institute of Chemical Sciences, Faculty of Chemistry, Maria Curie-Sklodowska University, Maria Curie-Sklodowska Sq. 3, 20-031 Lublin, Poland

Abstract

Ion-selective electrodes, due to many advantages, such as simplicity of use, low cost and high speed of measurements, as well as very good analytical parameters (low detection limits and high selectivity), have been widely used in recent years to determine various types of ions in environmental samples. Nitrates are ubiquitous in the environment, both in air, soil and water, and are essential for the proper growth of plants and animals. Research is still ongoing to unambiguously determine the influence of consumption of increased doses of nitrates on human health. Therefore, it is important to develop appropriate methods for determining their content in natural samples and in food products. The paper reviews articles on the latest knowledge on the influence of nitrates on human health as well as on the development and application of potentiometric sensors for determining the content of nitrates in environmental samples, including food products and various types of natural waters.

Keywords: nitrates, potentiometry, ion selective electrodes, solid contact

Nitrates are abundant in the natural environment, both in soil and water, as well as in all living organisms. They are also widely used by humans, inter alia, as artificial fertilizers to increase the yield of agricultural crops (Iammarino et al. 2013) and as preserving additives for meats and cold cuts, to improve the taste and color of products, inhibit the growth of bacteria and delay food spoilage as a result of rancidity (Bryan and Ivy 2015; Sindelar and Milkowski 2012).

Nitrates supplied to the body with food and drinking water are certainly very important biological compounds and have a good effect on human health. They have a protective effect on the cardiovascular system, lowering blood pressure and improving its flow in blood vessels (Sindelar and Milkowski 2012). Nitrates and nitrites are also nutrients necessary to maintain the homeostasis of nitric oxide (II) in the body, which, being a product of enzymatic synthesis, is involved in the process of wound healing and in the immune and neurological response (Bryan et Ivy 2015; Sindelar and Milkowski 2012). The fact that nitrates and nitrites are necessary in the human diet is also evidenced by, inter alia, the fact that in the early postpartum period in breast milk there is a relatively high concentration of these compounds, with the nitrite concentration outweighing the nitrate concentration, due to the absence of appropriate bacteria in the gastrointestinal tract of the newborn, which ensure the reduction of nitrates to nitrites. Later, however, this ratio is gradually reversed to the benefit of nitrates with obtaining appropriate commensal bacteria (Bryan et Ivy 2015).

In the right concentration, nitrates provide health benefits, but as with other chemicals, taking them in more than recommended amounts can have negative health effects, in this case mainly related to problems with the digestive system. Although nitrates have been used by humans for many different applications for centuries, the alarming results concerning the ill effects of increased doses of nitrates on human health resulting from numerous scientific studies conducted in the last century caused the use of nitrates to almost be banned in the 1970s, due to fears of carcinogenic nitrosamine formed during the thermal processing of meat products (Bedale et al. 2016). It was believed that their excessive consumption may also be associated with the occurrence of cancer and Parkinson's disease. At the beginning of the 20th century, research was also carried out on the so-called "blue baby syndrome", otherwise known as methaemoglobinaemia. The disease was expected to affect mainly infants and cause a significant reduction in the oxygen content in the blood of children (Alahi and Mukhopadhyay 2018; McKnight et al. 2009).

The main source of nitrates and nitrites in the human diet are vegetables and fruits, as well as, to a lesser extent, drinking water, animal products and grains. Nitrates are essential for the proper growth of plants, but the excess of nitrates absorbed by the plant, which the plant is no longer able to absorb, can accumulate in its tissues, especially in the leaves. Therefore, it is the leafy vegetables (lettuce, arugula, spinach, parsley) that contain the highest nitrate concentrations among various other vegetable species (Colla et al. 2018; McKnight and al. 2009). The content of nitrates in plant tissue may also be influenced by plant growth conditions (e.g. CO_2 content in the air, temperature and sunlight), as well as the harvest time and the conditions for their subsequent storage (Colla et al. 2018). The content of nitrates and nitrites in the body is due to both their consumption and their endogenous production due to the presence of denitrifying bacteria and oxidation of nitric oxide (II). The bioavailability of food nitrates is 100% (Bryan and Ivy 2015).

All nutrients should be supplied to the body in appropriate amounts so as not to cause negative health effects related to both their deficiency and excess. Also, nitrates and nitrites should be present in appropriate doses that enable proper growth and functioning. The increased content of nitrate ions has a negative effect on the balance in the environment and the proper functioning of living organisms. Therefore, in order to ensure the safety of humans and animals, it is necessary to monitor the state of the natural environment. For many essential vitamins as well as macro- and microelements, the optimal intake and the recommended diet for maintaining health and good condition of the body have been determined based on research. Therefore, governmental and international organizations have developed certain regulations to define and control the maximum concentration of nitrates in food and the environment (Alahi and Mukhopadhyay 2018). Recommendations established by the World Health Organization (WHO) allow a maximum concentration of nitrate in drinking water of 50 mg L^{-1} in Europe and 44 mg L^{-1} in the United States (Bryan and Ivy 2015), while the average daily nitrate intake was estimated at 43-141 mg. For nitrates and nitrites, optimal doses are much lower than harmful and lethal doses (Sindelar and Milkowski 2012).

According to scientists, the main risk of consuming increased levels of nitrates is their derivatives, such as nitrites, oxides and N-nitroso compounds (Colla et al. 2018). The nitrosation process is thought to be very important. There is S-nitrosation and N-nitrosation, the latter of which is harmful to the body and may result in the formation of carcinogenic compounds. According to scientists, however, this process does not occur under conditions of normal metabolism (Bryan et al. 2012). Although scientists currently claim that many civilizational diseases are mainly caused by poor nutrition, physical inactivity and stimulants, and there are no clear results of studies on the carcinogenic effect of nitrates in humans, not only in laboratory animals, there is still a need for further research and control of consumed nitrates in the diet. There are many review articles that collect research on the effects of nitrates and nitrites on animal organisms depending on the doses taken (Bedale et al. 2016; Bryan et al. 2012; Bryan and Ivy 2015; McKnight et al. 2009; Sindelar and Milkowski 2012).

Deviating from the subject of human health, poor management of available natural resources by people, excessive use of nitrate fertilizers in agriculture and the production of pollutants and waste also disturb the balance of the natural environment and the nitrogen cycle in nature by significantly increasing the concentration of nitrates and nitrites. Water is particularly susceptible to pollution, the purity of which should be particularly important to us nowadays. Too high concentration of nitrates in surface water bodies causes excessive growth of algae and phytoplankton, which contribute to the death of aquatic organisms that do not have access to dissolved oxygen in the water and to overgrowth of water bodies (eutrophication phenomenon) (Alahi and Mukhopadhyay 2018).

Concerns about the impact of increased consumption of nitrates and nitrites both on human health and the state of the natural environment made it very important to monitor their content in both the environment and in food products and drinking water. Therefore, it is important to develop effective, quick and accurate methods for determining the content of these ions in natural samples.

Scientists developed and implemented many analytical methods to determine nitrates in various types of natural samples, including spectrophotometry (Yue et al., 2004), gas chromatography (Akyüz and Ata 2009; Campanella et al. 2017), liquid chromatography (Akyüz and Ata 2009; Croitoru 2012), colorimetry (Woollard and Indyk 2014), spectrophotometry (García-Robledo et al. 2014), spectrofluorimetry (Biswas et al. 2004), amperometry (Can et al. 2012), voltammetry (Guadagnini and Tonelli 2013).

Potentiometric methods are often used to determine the concentration of nitrate ions in water samples because they allow for direct, quick and cheap measurements and do not require a complicated sample preparation process. In addition, potentiometric sensors with special parameters can be used for real-time and in situ research, which is particularly useful in monitoring the state of the natural environment. Ion-selective electrodes often show very good selectivity for selected main ions and they also reach lower and lower detection limits each year. In addition, the use of solids contact in ion-selective sensors, enabling the removal of the internal solution, allowed to increase the mechanical resistance of the electrodes, facilitate their storage and transport, and allowed for their miniaturization, which is particularly useful in the construction of multi-sensor platforms for applications in environmental measurements (Alahi and Mukhopadhyay 2018).

The first use of potentiometry for the determination of nitrate ions in water took place in the 1980s (Alahi and Mukhopadhyay 2018). Since then, there are still new research articles describing the innovative use of active substances and solid contacts, making it possible to obtain sensors with better and better analytical parameters.

In 2007, the Álvarez-Romero team constructed a potentiometric sensor using a composite material, polypyrrole doped with nitrate as recognition agent, to ensure selectivity for nitrate ions. The sensors obtained in this way were characterized by extended life time (~ 6 months) compared to unmodified electrodes and the possibility of regeneration of the sensor's active surface. Efficacy was tested in a real sample – in a drug (determination of isosorbide mononitrate, the active ingredient of Elantan) (Álvarez-Romero et al. 2007).

All-solid-state potentiometric sensors for nitrate determination using graphene as an ion-electron transducer were also constructed. The water layer test and impedance measurements were performed, confirming a significant reduction of the charge transfer resistance for the tested electrodes. In this way, sensors with a very good slope of the electrode characteristic curve (-57.9 mV / dec) and a fast response time (~ 10 s) were obtained, which were then successfully used to determine the nitrate content in drinking water samples (Tang et al. 2012).

Lipophilic multiwalled carbon nanotubes (f-MWCNT) were also used as the ion-electron transducer placed between the solid electrode material and the ion-selective membrane layer. According to the authors, the obtained sensors showed many advantages, such as insensitivity to pressure and light, the possibility of vertical or horizontal orientation, and high mechanical and chemical strength, which may be particularly useful in the construction of multi-sensor research platforms for determining the content of selected ions in the environment in situ (Yuan et al. 2015).

An interesting solution was proposed by scientists from the Garland team, who used laser induced graphene (LIG) as an innovative way to produce ion-selective electrodes. According to the authors, it is to be a one-step, easy and cheap process of producing laser recording on polyamide substrates, which can then be used for scalable roll production and disposable sensors in technologies. The publication focuses on the determination of nitrogen available to plants in soil in the form of both nitrate (NO_3^-) and ammonium (NH_4^+) (Garland et al. 2018).

Again, in order to test soil samples, sensors were constructed using a novel nanocomposite of poly(3-octyl-thiophene) and molybdenum disulfide (POT-MoS_2) as a solid contact layer. The nanocomposite is characterized by high hydrophobicity and redox properties. Based on the research, it was found that the modification of the POT chain with MoS_2 increased both the conductivity and the anion exchange, and minimized the formation of a water layer at the interface between the ion-selective membrane and the substrate (in this case, the Au electrode). The purpose of the sensor is long-term use and continuous monitoring of nitrate content in the soil (Ali et al. 2019).

Sensors with very good stability, repeatability and potential reproducibility were produced by using platinum nanoparticles on a carbon black support (Pt-NPs-CB) as solid contact. The research used chronopotentiometry with current reversal and the potentiometric test of the water layer. Additionally, the use of this type of transducer made it possible to significantly reduce the resistance of the ion-selective membrane (Paczosa-Bator et al. 2013).

The use of the association complex of nitron-nitrate ions (Nit^+/NO_3^-) and multi-wall carbon nanotubes (MWCNT) as an intermediate layer between the ion-selective membrane (ISM) and the glassy carbon substrate made it possible to significantly reduce the potential drift after modification and over 10-fold increase in double layer capacitance compared to a conventional ion selective electrode. The generated sensors were successfully used to test real samples for the presence of nitrate ions – wastewater, fertilizers and gun powder samples (Hassan et al. 2019).

Another method of obtaining ion-selective electrodes sensitive to nitrate ions was electropolymerization of N-methylpyrrole with the use of potassium nitrate as an auxiliary electrolyte by the Bomar research team. It has been found that N-methylpyrrole is better than pyrrole for this purpose, and electrodes with an ionic imprinted polymer exhibit very good selectivity and stability of potential and a long lifetime (Bomar et al. 2017).

The electrodes were also constructed with a graphene-tetrathiafulvalene interlayer acting as a solid contact. The use of graphene allowed to obtain a much lower resistance of the ion-selective membrane and a potential drift compared to the unmodified electrode. In this case, the best parameters were obtained for the electrode modified with GR-TTF(NO_3) nanocomposite (Pi k et al. 2016).

A completely new active substance used in the ion-selective electrodes was a cobalt(II) complex with 4,7-diphenyl-1,10-phenanthroline (Bphen) with the formula $Co(Bphen)_2(NO_3)_2(H_2O)_2$. The obtained sensor with simple operation and construction, without an additional intermediate layer, which was characterized by very good analytical parameters, a wide measuring range and pH range in which the sensors could work (5.4 – 10.6), fast response time and very good potential stability. The electrodes worked properly for many months. Their practical application has been checked in the determination of nitrate ions in natural samples: water (mineral, tap and river water) and in vegetables (Pietrzak et al. 2020).

In order to improve the analytical parameters of the electrodes, an addition of ionic liquid (IL) – trihexyltetradecylphosphonium chloride (THTDPCl) was also used as a component of the ion-selective membrane consisting of polyvinyl chloride (PVC) and a plasticizer (NPOE). The ionic liquid played a very important role in this case, both the ionophores and the ionic lipophilic component reducing the resistance of the ion-selective membrane, as well as the converter aimed at stabilizing the potential of the internal electrode. It is an inexpensive and easy to manufacture sensor with good potential stability and selectivity. It was used in samples of water and vegetables, in which the content of nitrate ions was successfully determined (Wardak 2014).

Table 1. presents a summary of analytical parameters for selected sensors sensitive to nitrate ions, which have been described in the literature over the last 15 years.

Table 1. Comparison of basic analytical parameters of nitrate ion-selective electrodes with solid contact.

Active substance	**Contact**	**Slope [mV/ dec]**	**LOD [mol L^{-1}]**	**Linear range [mol L^{-1}]**	**Response time [s]**	**Life time [months]**	**Refence**
Ppy(NO_3^-) composite	graphite powder	-57.1	5.4×10^{-5}	$1.5\times10^{-4} - 1.0\times10^{-1}$	20	~6	(Álvarez-Romero et al., 2007)
MTDDA-NO_3	graphene	-57.9	3.0×10^{-5}	$5.0\times10^{-5} - 1.0\times10^{-1}$	~10	-	(Tang et al., 2012)
TDMAN	f-MW-CNTs	-57.7	2.5×10^{-6}	$3.2\times10^{-6} - 1.0\times10^{-1}$	-	-	(Yuan et al., 2015)
TDMAN	laser induced graphene	-54.8	2.1×10^{-5}	$5.0\times10^{-5} - 1.0\times10^{-1}$	-	-	(Garland et al., 2018)
TDMAN	POT-MoS_2 nanocomposite	-64.0	9.2×10^{-5}	$7.1\times10^{-4} - 1.0\times10^{-1}$	-	-	(Ali et al., 2019)
TDMAN	PtNPs-CB	-58.6	5.0×10^{-7}	$1.0\times10^{-6} - 1.0\times10^{-1}$	5	~5	(Paczosa-Bator et al., 2013)
(Nit+/ NO_3–) complex	MWCNTs	-55.1	2.8×10^{-8}	$8.0\times10^{-8} - 1.0\times10^{-2}$	<10	2	(Hassan et al., 2019)
poly(N-methylpyrrole)	-	-56.3	2.8×10^{-8}	$5.0\times10^{-6} - 1.0\times10^{-1}$	-	6	(Bomar et al., 2017)
nitrate ionophore V,	TTF(NO_3)	-59,4	6.3×10^{-7}	$1.0\times10^{-6} - 1.0\times10^{-1}$	-	-	(Pięk et al., 2015)

Active substance	Contact	Slope [mV/dec]	LOD [mol L^{-1}]	Linear range [mol L^{-1}]	Response time [s]	Life time [months]	Refence
nitrate ionophore V,	GR-TTF	-59.1	6.3×10^{-7}	1.0×10^{-6} – 1.0×10^{-1}	-	-	(Pięk et al., 2016)
$Co(Bphen)_2(NO_3)_2$	Ag/AgCl/Cl^-	-56.3	4.0×10^{-6}	1.0×10^{-5} – 1.0×10^{-1}	-	> 3	(Pietrzak et al., 2020)
THTDPCl	Ag/AgCl/Cl^-	-60.1	2.8×10^{-6}	1.0×10^{-5} – 1.0×10^{-1}	5-10	> 4	(Wardak, 2014)

LOD – limit of detection;
MTDDA-NO_3- methyltridodecylammonium nitrate,
TTF-TCNQ – tetrathiafulvalene-tetracyanoquinodimethane;
f-MWCNTs – lipophilic multiwalled carbon nanotubes;
TDMAN – tridodecylmethylaminium nitrate;
THTDPCl – trihexyl- tetradecylphosphonium chloride;
Ppy(NO_3^-) composite – composite comprising graphite powder, polypyrrole doped with nitrate and epoxy resin;
CRGNO – chemically reduced graphene oxide;
PtNPs-CB – carbon black supporting platinum nanoparticles;
(Nit^+/NO_3^-) – nitron-nitrate ion association complex;
GR-TTF – graphene–tetrathiafulvalene nanocomposite;
TDMACl – tridodecylmethylammonium chloride;

Table 2 shows examples of the application of solid contact ISEs for the determination of nitrates in natural samples, e.g. in various water samples and vegetables using ion-selective electrodes.

Table 2. Examples of application of solid contact ISEs for the determination of nitrates in real samples.

Type of ISE (solid contact/inner electrode)	Sample	Method	Ref
Graphene/GCE	Mineral water Tap water	Calibration curve	(Tang et al., 2012)
TTF/NO_3^-/GCE	Ground water Well water Tap water River water	Calibration curve	(Piek et al. 2015)

Type of ISE (solid contact/inner electrode)	Sample	Method	Ref
Ionic liquid(TDMACl)/ Ag/AgCl	Mineral water Tap water	Multiple standard addition	(Wardak et Grabarczyk, 2016)
	Vegetables (Iceberg lettuce Butterhead lettuce Fresh spinach)	Multiple standard addition	
MWCNTs/GCE	Waste waters (Aerated lagoon effluent, Raw sewage plant inflo, Nitrate fertilizer factory, outfalls)	Calibration curve	(Hassan et al., 2019)
Ionic liquid(TDMACl)/ Ag/AgCl	Tap water Mineral water River water	Calibration curve	(Pietrzak et al., 2020)

Recently our team developed all solid state nitrate ion-selective electrodes in which ionic liquid and multiwalled carbon nanotubes were used as additional membrane components (Pietrzak and Wardak 2020). Such modification of membrane composition caused noticeable improvement in the electrode performance, especially in potential stability and reversibility. The electrode with the best analytical parameters was successfully used for nitrate determination in natural waters samples (water from Bystrzyca River and Zemorzyce Lake) and vegetables. The water samples were analyzed without pretreatment, whereas vegetables were analyzed after minimum sample preparation without mineralization. They were collected from local markets during the period of March –April 2019. A 5g portion of previously homogenized vegetable samples was mixed with deionized water and the mixtures were stirred and heated (80 °C) for 30 min. After cooling the solutions were transferred to a 500 mL volumetric flask and diluted to volume with deionized water.

Potentiometric measurements of electromotive force (EMF) were performed in a two-electrode system with an ion-selective electrode sensitive to nitrate ions (NO_3-SCISE) as an electrode working against a silver-chloride electrode as a reference electrode. The determination of nitrate was performed by the standard addition method. Recovery was also examined. Obtained results are presented in Table 3 where it can be seen that our electrode is suitable for nitrate monitoring in environmental samples.

Table 3. Result of nitrates determination in various samples (unspiked and spiked) using nitrate ion-selective electrode.

Sample	Nitrate found by NO_3^-SCISE, mg L^{-1} or mg kg^{-1}	Recovery, %
River water	14.6±0.4	-
River water +50 mg L^{-1} NO_3^-	65.2±0.6	100.9
Lake water	17.2±0.7	-
Lake water +50 mg L^{-1} NO_3^-	66.8±1.1	99.4
butterhead lettuce	916 ± 18	-
butterhead lettuce + 300 mg kg^{-1} NO_3^-	1226 ± 23	100.8
Radish	396 ± 16	-
Radish +300 mg kg^{-1} NO_3^-	732 ± 19	105
Fresh spinach	1322 ± 11	-
Fresh spinach + 300 mg kg^{-1} NO_3^-	1546 ± 13	95.3
Cucumber	532 ± 23	-
Cucumber + 300 mg kg^{-1} NO_3^-	815 ± 27	97.9
Cabbage	312 ± 23	-
Cabbage + 300 mg kg^{-1} NO_3^-	612 ± 22	100
Tomato	414 ± 16	-
Tomato + 300 mg kg^{-1} NO_3^-	688 ± 27	96.4

Conclusions

Ion-selective electrodes are a cheap and simple analytical tool for determination of many ions in environmental samples, including nitrates. In recent years scientists constructed many types of ion-selective electrodes with lower and lower detection limits and better potential stability, at the same time with very good selectivity, which is a special feature of ion-selective electrodes. This creates more and more possibilities to monitor nitrate in the environment in different samples, also online.

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