NITRITES, NITRATES AND AMMONIUM MONITORING IN CRISUL REPEDE RIVER AND PETA, ORADEA AREA

Alexandrina Fodor*, Petrehele Anda Ioana Gra□iela*, Chi□Adriana, Purcarea Cornelia****

**University of Oradea, Science Faculty, Chemistry Department, 1 Universitati St., 410070 Oradea; Romania, afodor@uoradea.ro*
**University of Oradea, Faculty of Environmental Protection, 26 gen. Magheru St., 410048 Oradea; Romania

Abstract
The nitrites, nitrates and ammonium monitoring, using spectrophotometric methods, for the Crisul Repede River waters (upstream and downstream of Oradea and Peta) during four months: January, February, March and April-2009 show that the potable water source of Oradea town correspond with the potability requirements from Legea 458/2002 modified and filled -Legea 311- June 28, 2004 concerning the potable water quality. Breaks of this established limits was recorded just in ammonium case in downstream Peta zone through that study period, and this break can be explained with the organic compounds pollution.

Key words*:* nitrite, nitrate, ammonium, spectrophotometric determination

INTRODUCTION

The water represent a regenerable, vulnerable and limited natural source, an indispensable substance to our existence, for society, prime material for productive activities, energie source and a water way and decisive element in the ecological equilibrium maintenance. Water is not nobodies domain, it is a integrated part of the public domain. Among toxics circulating in water, a part are having natural origin, but most of them results from aquifers pollution. Nitrates (NO_3^-) can constitute a majore problem, their concentration in the drinkable water above admisible limits being frequent in our country. In vegetables the nitrates are powerfully concentrated (Manescu and all., 1982). Nitrates are noxious just in very big concentrations and this cases are rare in water. Noxious are in fact the nitrites which results from nitrates in certain conditions, in organism but abiotic too in reservoir and zinc pipes where the nitrates are reduced to nitrites generating a secondary toxicity of nitrates. The nitrites(NO_2^-) are resulting from nitrates or before consume or in the lumen of alimentary canal, in migration case, in divers circumstances, to stomach and small intestine of reducing elements from intestinal biocenose. The consequence is methemoglobinemia which is affecting the young ages, but sometimes the adults too, such as those with gastric resection (Mare, 1973; Mertz and Cornatzer, 1971; Lassiter and all., 1978). The susceptibility to nitrites, for new born children and animals is due to the fetal hemoglobin which has more affinity for oxygen therefore form met hemoglobin quicker then adults (WHO, 2007). The children under three months are more expose to methemoglobin because of the less citochrome NADH activity which reconvert methemoglobine back to hemoglobin and also because the high risk for intestinal (Savino et al. 2006). Some of thouse infections were signalize in the last years in Italy (Matteucci et al., 2008 şi Savino et al., 2006), Spain (Sanchez-Echaniz et al., 2006) and Australia (Maric et al., 2008).

The methemoglobinizant effect were studied in our country in Transilvania area (Zeman et al., 2002) on an 71 children group feed with powder milk made using drilled fountain water. It was demonstrate in more cases that the diarrhea has a great influence on methemoglobinemiei. Our country is having a high incidence of methemoglobinemia with a significant death rate. In 1984-1995 was recorded 2346 cases of methemoglobinemia at children under 1 year and at 80 deceases. We have signs that the numbers are underestimated because of the diagnosis difficulties. The source is the water fecaloid contamination too, but morbidity rised powerfuly mostly because of the usage on large-scale of fertilized substances in agriculture. In 1988 36% from the Romania's fountains had nitrate concetrations over 45 mg / l (Medium Protection, Water Quality, II edition, 2004). This essay have as purpose the quantitative determination of nitrates, nitrites and ammonium from de surface water. I choiced as sections downstream Crisul Repede and upstream Oradea, and river Peta because this are the main drinkible water source of Bihor county. The present STAS was published in the Monitorul Oficial al României on July 29 2002 and which regularize the drinkible water quality, having as an objective the people health protection against the effects of any drinkible water contamination type through her quality insurance of clean and healty water, law which was modified and filled in by Legea 311/2005.

MATERIAL AND METHODS

The method principle for nitrites (NO_2^-) content determination is the nitrate ions reaction present in test, at pH=1,9 with *4-amino benzene sulfonamide* reagent in the *orthophosphoric acid* to form *diazonium salt* which form a red colour complex with *N(1-Naphthyl) ethylene diamine dihydrochloride* (help by *4-amino benzene sulfonamide reagent*). It must be measured the absorbance at 540 nm (Ghimicescu and Hincu, 1974; Manescu and all, 1982). The method is applied to direct determination of nitrite ion from de surface waters, subsurface waters and thread waters. It can be determinate an azote concetration from nitrites until 0.25 mg/l. It was used the UV-VIS ATI-Unicam UV-VIS 2-300 spectophotometer. The itrates (NO_3^-) content determination around spectometric measuring of yellow compound absorbance formed through *sulphosalicylic acid* reaction (formed through addition at probe of sodium salicylate and sulphuric acid) with nitrate, followed by alcaline solution treatment. Disodium salt of *ethylene diamine tetra acetic acid* (*EDTA*Na_2) is added to alcaine solution for prevent precipitation of calcium and magnezium salt. *Sodium azide* is added to remove interference with nitries. The method is applied for nitrate concentrations, less then 0,2 mg/l using a probe volume for analize maximally 25 ml (Ghimicescu and Hincu, 1974; Manescu and all, 1982).

The measurment was effectuated using UV-VIS Unicam EM 12.0 molecular absorption spectometer. Ammonium (NH_4^+) content determination around spectometric measuring at λ=655nm of blue colored complex formed through ammonium reaction with *salicylate ions* and *hipochloride* in presence of *sodium nitroprusside*. *Hipochloride ions* are generated through alcaline hydrolysis of sodium salt *N,N'- dichloro -1,3,5-triazine - 2,4,6(1H,3H,5H)- trione* **(***Sodium Dichloroisocyanurate***).** *Chloramine* reaction with *sodium salicylate* have place at pH=12.6 in the presence of *sodium nitroprusside*. *Sodium citrate* is added for for interference dissimulation gived by cation, in special by calcium and magnezium (Ghimicescu and Hincu, 1974; Manescu and all, 1982). It was used UV-VIS Unicam EM 12.0 molecular absorption spectometer.

Table 1

The limit values for the compounds with nitrogen from the surface waters according to his category (European Law, Water Surces 2002)

	CLS.I	CLS II	CLS III	CLS IV	CLS V
N-NH_4 mg/l	0,2	0,3	0,6	1,5	> 1.5
N-NO_2 mg/l	0,01	0,06	0,12	0,3	> 0,3
N-NO_3 mg/l	1	3	6	15	> 15
N total mg/l	1,5	4	8	20	> 20

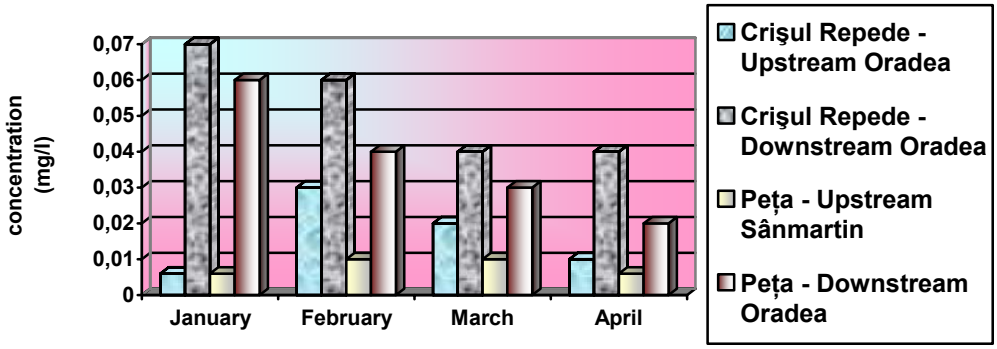

Fig. 1 Nitrites composition (STAS SR EN 26777/02)

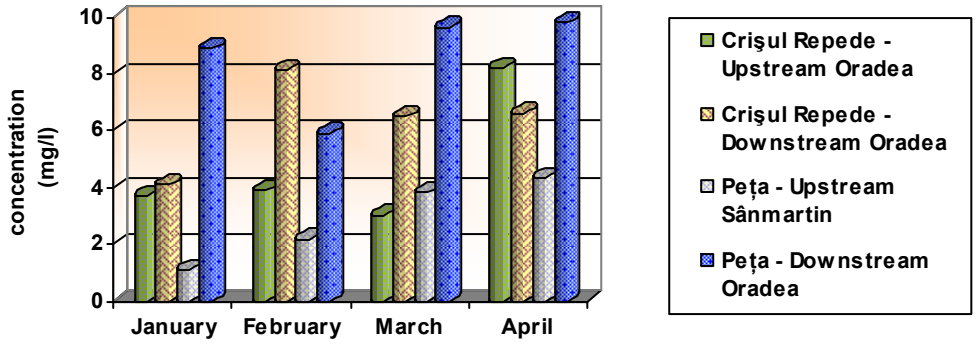

Fig. 2 Nitrates composition (STAS SR ISI 7890-1)

In conformity with Act 311/04 the maximum admitted nitrate quantity is 50 mg/l and from the graphic we observe that in all of the section presented the nitrates concentrations are under the permeated values. The determination method was STAS SR ISO 7890: 3:2000. The obtained results on ammoniac determination are presented in figure 3.

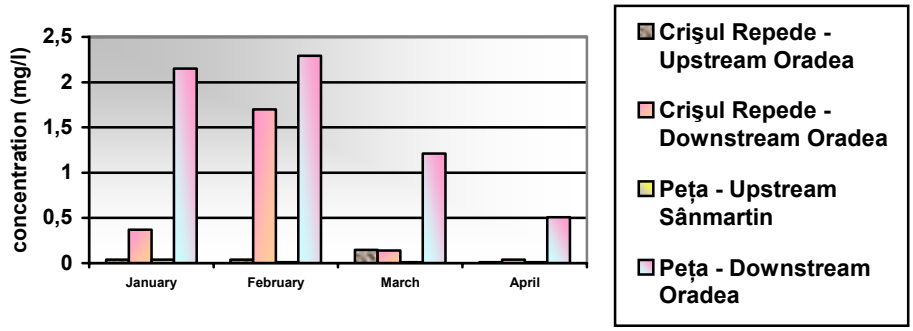

*Fig. 3*Ammonium composition (STAS SR ISO 7150-1/ 2001)

CONCLUSIONS

The graphic for the nitrites determination show that the nitrites concentrations are in every section under the maximum admitted concentrations (0,5mg/l), specified value in the Water Act 311/04, during the all studied period.

In conformity with Act 311/04 the maximum admitted nitrate quantity is 50 mg/l and from the graphic we observed that in all of the section presented the nitrates concentrations are under the permeated values.

In conformity with Act 311/04 the maximum concentration admitted for ammonia is 0,5 mg/l. From the graphic it can be observed that in Peţa- Downstream Oradea the ammonia concentration is higher then the permitted value every month. An explanation the can be given is the pollution with organic compounds.

REFERENCES

1. .European Law, Water Surces , (2002). Ed. HGA, Bucureşti, 55 pp.
2. Ghimicescu G., I. Hincu, 1974, Chimia si controlul poluarii apei, Ed. Tehnica, Bucuresti.
3. Lassiter J. W., E. Abrams, J. Miller , 1978, Proc. Int. Syimp. On Trace Element, 4.
4. .Manescu S., H. Dumitrescu , Z. Barduta , M.L. Diaconescu , 1982, Chimia sanitara a mediului, II, Ed. Medicala, Bucuresti.
5. Mare L., 1973, Les oligoelements en nutrition humaine, Rapp. Tech., OMS Geneve, 54.
6. Maric P., S.S. Ali, L.G. Heron, , D. Rosenfeld, M. Greenwood, 2008, Methemoglobinemia following ingestion of a commonly availeble food additive, Med. J. Aust., 188(3), 156-158.
7. .Matteucci, O., G. Diletti, V. Precipe, E. Giannatale, M.M. Marconi, G. Miglorati, 2008, Two cases of methemoglobinemia caused by suspected sodium nitrite poisoning. Veterinaria Italiana, 44(2), p 439-453.
8. Medium Protection, Water Quality, II edition, 2004, European Institute Romania.
9. .Mertz, W. , E. Cornatzer, 1971, Trace. Elements in nutrition, N. Y. Deker Ed., 123.
10. Sanchez-Echaniz J., J. Benito-Fernandez, S. Mintegui-Raso, 2001, Methemoglobinemia and consumption of vegetables in infants. Pediatrics., 107(5), 1024-1028 .
11. .Patroescu C., I. Ganescu , 1980, Analiza apelor, Ed. Scrisul Romanesc, Craiova.
12. .Savino F., S. Maccario, C.Guide, E. Castagno, D.Farinasso, F.Cresi, L. Silvestro, G.C. Mussa, 2006, Methemoglobinemia caused by ingestion of courgette soup given to resolve constipation in two formula-fed infant. Ann. Nutr.Metab, 50, 368-371.
13. STAS SR EN 26777/02.
14. STAS SR ISI 7890-1.
15. STAS SR ISO 7150-1/ 2001.