Asian Journal of Chemistry Vol. 21, No. 4 (2009), 2695-2699

Determination of Cr(III) and Cr(VI) Concentrations of the Jiu and Olt Rivers of Romania

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This paper presents a comparative study of Cr(III) and Cr(VI) distribution on Jiu and Olt rivers. The concentration of Cr(III) and Cr(VI) in Jiu river were determined using inductively coupled plasma mass spectrometry while for Olt river by atomic absorption spectrometry.

Key Words: Chromium(III), Chromium(VI), Jiu river, Olt river, ICP-MS, AAS.

INTRODUCTION

Jiu river is an important river of southern Romania. It is formed near Petrosani by the junction of headwaters Western Jiu which springs from the Retezat Mountains and Eastern Jiu which springs from the Parang Mountains. The significant point pollution sources are the agglomerations which are discharging untreated urban wastewaters or only mechanically treated and the industrial companies (chemical, mining, oil-chemical, machine construction, food, *etc.*). The main polluters within the Jiu hydrographical basin are: Craiova City, Doljchim Craiova, Lupeni and Petrila mine dressings[1].

Olt river is another important river of Romania which length is 670 km. Its source is in the Hasmasul Mare Mountain of the eastern Carpathians Mountains, Oriental Carpathians. It flows through Romanian counties Harghita, Covasna, Brasov, Sibiu, Valcea and Olt. Sfantu Gheorghe, Ramnicu Valcea and Slatina are the main cities on the Olt Rive course. It is the largest and longest Romanian tributary of the Danube river. Olt river flows into the Danube river near Turnu Magurele. In general, the pollution by stationary sources is mainly generated by the communal economy activities, chemical industry and zootechnics followed by the economic units within the ore mining and metalworks. The main stationary sources of pollution within this hydrographical basin, area Valcea are the following industries: chemical Oltchim Ramnicu Valcea, pulp and paper, extractive and communal economy activities (Brasov, Sibiu, Rm. Valcea and Slatina).

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In this paper, the concentrations of Cr(III) and Cr(VI) present in Jiu river were determined using inductively coupled plasma mass spectrometry (ICP-MS). The contents of Cr(III) and Cr(VI) collected from various points of Olt river were analyzed by the atomic absorption spectrometry.

EXPERIMENTAL

For Jiu river, the samples have been taken in three months, June and November 2006 and February 2007, representing the summer, the autumn and the winter, from 6 different points of the Jiu river. These points were: (1) Campului Neag (The West Jiu); (2) Livezeni (The East Jiu); (3) upstream the confluence with Sadu; (4) Podari; (5) Malu Mare and (6) Zaval, the point where Jiu river flows into the Danube river. Malu Mare is the point where wastewater from Craiova, the biggest city on Jiu river course overflows into Jiu river.

For Olt river, the samples were collected also during three months, June and November 2006 and February 2007, which represent three seasons: the summer, the autumn and the winter, from 7 points of Olt river long ways of Valcea County. These points were: (1') Boita; (2') Cornet; (3') Ramnicu Valcea; (4') Tatarani; (5') Cremenari; (6') Dragasani; (7') Strejesti.

The distance from the river side was about 2.00-2.50 meters and the depth was about 0.20-0.50 meter. Water samples were collected manually into polyethylene bottles. Prior to use, all bottles were cleaned with 10 % HNO_3, rinsed with distilled water and after that, with the water to be analyzed[2]. Before the analysis, the sample was filtrated and it hadn't been mineralized. The analysis of Jiu river water was made by using inductively coupled plasma mass spectrometry (ICP-MS-Quadrupole Mass Analyzer, AGILENT 7500).

The measurements of Cr(III) and Cr(VI) concentration on Olt river were estimated using atomic absorption spectrometry (NOVAA 300-Analytic Jena). The working temperature range varies from + 10 to 35 ºC. The humidity is max. 90 % at + 30 ºC and the storage temperature (drying agent) is from -40 to + 50 ºC.

RESULTS AND DISCUSSION

Table-1 presented the highest concentration levels admitted by Romanian standards for Cr(III) and Cr(VI) ions[8]. The quality classes are: I = very good; II = good; III = moderate; IV = satisfactory; V = weak.

TABLE-1
CONCENTRATIONS FOR Cr(III) AND Cr(VI) AS ADMISSIBLE BY ROMANIAN STANDARD

Metals	Measure units	Concentrations values-Romanian standard				
		I	II	III	IV	V
Cr (Cr^{3+} and Cr^{6+})	µg/L	25	50	100	250	> 250

For Cr^{3+} the highest concentrations admissible is Cr^{3+} = 500 μg/L and for Cr^{6+} the highest concentrations admitted is Cr^{6+} = 50 μg/L.

Fig. 1 shows the variation of the concentration of the Cr(III) in the samples taken from the Jiu river. The measurements show that in all points of harvesting the concentration of Cr(III) is below the admitted limit, but in June 2006, in Malu Mare point, the concentration of Cr(III) is higher than the concentration of Cr(III) in other points. As it has been shown Malu Mare is the point where are discharged wastewaters from Craiova city.

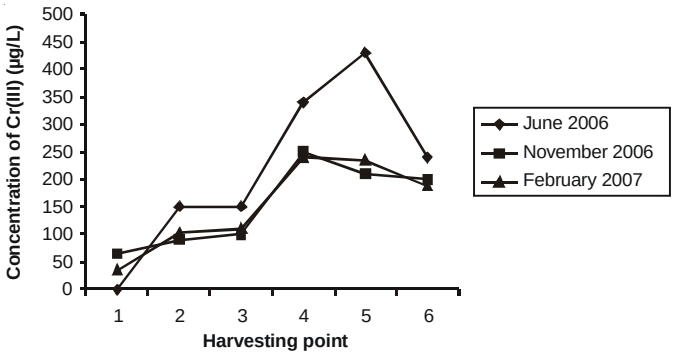

Fig. 1. Variation of the concentration of Cr(III) in the samples taken from the Jiu river

Fig. 2 shows the variation of the concentration of the Cr(III) in the samples taken during the three seasons from the Olt river.

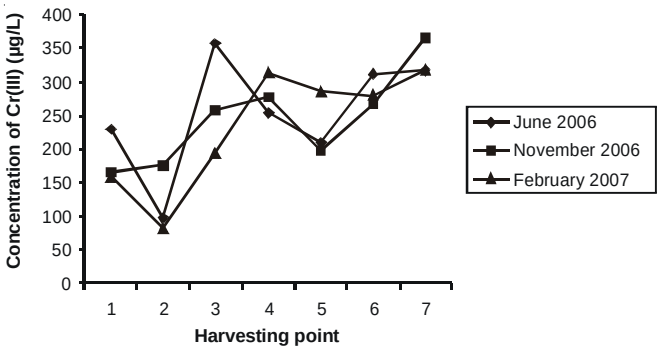

Fig. 2. Variation of the concentration of Cr(III) in the samples taken from the Olt river

In June 2006, it can be seen that at Rm. Valcea and at Strejesti, the concentration of Cr(III) increases but less than the admissible limit. Also, in November 2006, in Strejesti point the concentration of Cr(III) is higher than in other points. In February 2007, the concentration of Cr(III) grows relatively constantly.

Fig. 3 shows the variation of the concentration of Cr(VI) in the samples taken from the Jiu river. As it can be seen in the three seasons, the concentration of Cr(VI)

grows constantly, from the source towards the flowing point. In Malu Mare point, in June 2006 and in February 2007, the concentration of Cr(VI) is more than the admissible concentration.

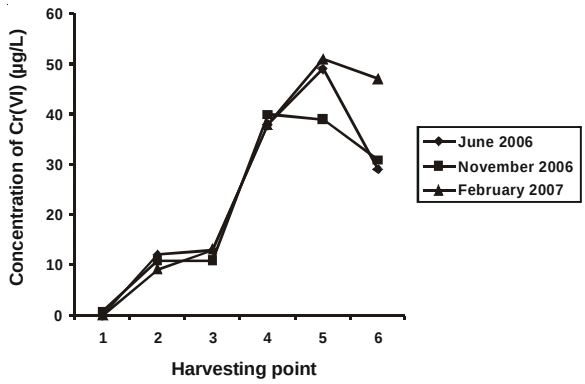

Fig. 3. Variation of the concentration of Cr(VI) in the samples taken from the Jiu river

Fig. 4 shows the variation of the concentration of the Cr(VI) in the samples taken during the three seasons from the Olt river. The measurements show that the concentration of Cr(VI) is higher in Rm. Valcea and Dragasani points. Rm. Valcea and Dragasani are two cities from southern Romania where several leather manufacturing units use Cr(VI) as pigments.

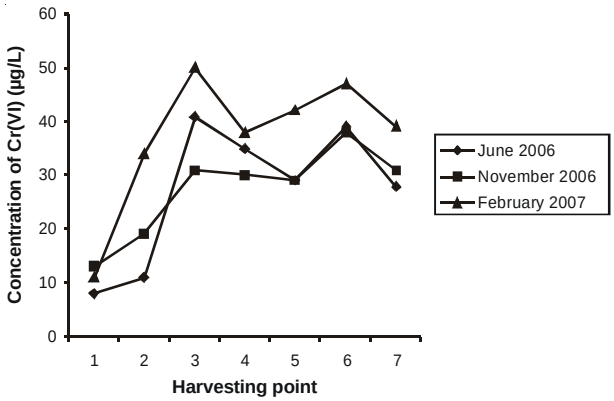

Fig. 4. Variation of the concentration of Cr(VI) in the samples taken from the Olt river

Conclusion

Due to the industry established along the Olt river, the concentrations of Cr(III) and Cr(VI) are higher than the concentrations of these ions on the Jiu river course, but are below the admitted limit. In one place, in Malu Mare point, the concentration of Cr(VI) is higher on the Jiu river course than on the Olt river course. In this point

are discharged wastewaters from Craiova city, the biggest city in this area. Craiova has many places of leather manufacturing units. Inadequate management of municipal wastewater is one of the core problems in the Jiu river basin.

The chemical, food and pulp and paper industries are among the main industrial polluters in the Olt river basin. Discharges from such plants significantly raise the levels of Cr(III) and Cr(VI) in the river network.

Table-2 presented a comparison between the precision of these two methods concerning Cr(III) and Cr(VI) analyzed. As can be seen, the determination of trace metals in a chemical plant wastewater effluent might be conducted most efficiently with a multielement technique such as ICP-MS.

TABLE-2
COMPARISON OF DETECTION LIMITS IN µg/L

Heavy metal	The precision	
	ICP-MS	AAS
Chromium	< 0.005	< 10

The results of this study showed that Jiu and Olt rivers water are in the first and second quality class from the viewpoint of Cr(III) and Cr(VI).

ACKNOWLEDGEMENTS

This work was supported in part by the National University Research Council -CNCSIS, Romania, under the research projects 621/2007-2008: "Advanced procedures for modelling, identification and nonlinear control of biochemical and biotechnological processes for water quality improvement" and ID786/2007-2010: "Methods and algorithms for continuous time non-linear systems identification".

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(*Received*: 24 March 2008; *Accepted*: 10 January 2009) AJC-7107