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### A CHEMOMETRIC STUDY OF THE WATERS OF DANUBE RIVER ALONG THE ROMANIAN TERRITORY

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The Danube, one of Europe's main rivers, covers 1,075 Km of the Romanian territory, forming Romania's border with Bulgaria and Yugoslavia.

Interpretation of the huge amount of data obtained by a permanent monitoring of the Danube's waters involved multivariate chemometrical methods -factor analysis and cluster analysis [1,2]. Our paper employed the data collected, ten months a year, along seven years of observation (1990-1996). The samples taken over have been subjected to very strict chemical analyses, a total number of 19 variables being studied as follows: pH, organic carbon, hardness, residues, suspensions, alkalinity, carbonates, nitrites, nitrates, etc.

For a thorough analyses, both chemical and instrumental methods (such as flame photometry, electroanalytical and turbidimetric procedures) have been applied. The dendograms' interpretation (based on Euclidean metrics) evidenced the stability of all variables subjected to observations for seven years. It was only the pH (and the variables correlated with it) that showed variation along one of the years of observation, which may be explained either through the influence of some climatic factors or through certain polluting effects. Finally, significant correlation could be established between the Danube water's composition and the living conditions of some fish species.

The paper discusses both the dendograms obtained by processing data from each of seven years of monitoring, and the scatterplots.

[1] A. Mackiewicz and W. Ratajczak, *Principal Components Analysis, Computers and Geosciences*, 19, (3), p. 303-342, 1993.

[2] T.P.E. Auf der Heyd, *Analyzing Chemical Data in More than Two Dimension*, J. Chem. Educ., 67, (6), 1990

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### DETERMINATION OF LEAD AND CADMIUM IN SOFT AND DURUM WHEAT BY DERIVATIVE POTENTIOMETRIC STRIPPING ANALYSIS

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Lead and cadmium play a primary role between heavy metals, since, owing to their metabolic inertness, they are permanently retained giving rise to the bio-accumulation phenomenon that causes severe consequences for human health. FAO/WHO fixed an allowable weekly intake of 0.4-0.5 ppm of cadmium and 3 ppm of lead for the adult<sup>2,3</sup>. The determination of lead and cadmium in soft and durum wheat is important owing to the both nutritional interest and incidence in the diet of these foodstuffs. Flame and graphite furnace atomic absorption spectrophotometric techniques, as well as electroanalytical such as pulsed techniques, are frequently used<sup>4-6</sup>.

In this paper potentiometric stripping analysis (PSA) was employed. PSA is a relatively new electroanalytical technique first proposed by Bruckenstein and Bixler<sup>7</sup> and further developed by Jagner and Graneli<sup>8</sup>. PSA is a two-step technique. The first step (preconcentration) is an electrolysis of the solution containing the ions of the metals under examination, which are amalgamated on a mercury-coated glassy carbon electrode. The second step (stripping) is a chemical re-oxidation of the deposited metals. When the potential (E) and time (t) data are digitally converted into dt/dE and dt/dE is plotted against E, the sensitivity of the method can be increased and the resolution improved. Accuracy of the method is 98-101% with a standard deviation of 3-5%. The detection limit is of the order of 0.1 ppb for both analytes, depending on deposition time. In the samples so far examined the concentrations were up to 200 ppb for cadmium and up to 400 ppb for lead.

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### ANALYTICAL APPLICATION OF EXTRACTION IN NI (II) - NITROSONAPHTHOLE - CYANINE DYES SYSTEM

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Complex formation of Ni (II) with nitrosonaphthols (HA) and cyanine dyes (R<sup>+</sup>) has been studied by means of spectrophotometric method. It has been found that in neutral and alkaline solutions chelate complexes of MA<sub>3</sub> type are produced. They are readily extracted with R<sup>+</sup> in the form of extensively dyed ion associated (IA) into lowpolar organic solvents. The influence of medium acidity, nature and concentration of nitrosonaphthols, cyanine dyes, solvents and other factors on complex formation and extraction of IA has been studied.

Maximum yield of IA is observed while using 1-nitroso-2-naphthole as HA, dimethylindocarbocyanine (DIC) and dimethylidodicarbocyanine (DIDC) as a cyanine dye and toluene (or benzene) as an organic solvent.

The optimal medium for nickel IA formation and extraction is pH 7.5-10. The IA composition and structure have been determined by various spectrophotometric methods as well as by studying IR-spectra of the compounds extracted. The ratio metal: ligand: cyanine dye is equal to 1:3:1, the extracted IA corresponding to the general formula [MA<sub>3</sub>]xR<sup>+</sup>S (where S is an organic solvent). The extraction power of solvents in the series benzene>toluene>o,p,m-xylol> ethylbenzene> butylbenzene>CCl<sub>4</sub>>>hexane, octane, heptane. Spectrophotometric parameters of IA metals with high value (0.7-1.5)×10<sup>5</sup> of molar absorption coefficients have been calculated from electronic absorption. On the basis of the data obtained highly sensitive and selective methods of nickel extraction-photometric determination the traces (DL 10<sup>-2</sup> mg/l) of these metal in drinking water and electroplating wastes are suggested.

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### CATALYTIC TITRATIONS BY THE APPLICATION OF IODIDE-CATALYSED MANGANESE(IV)-ARSENIC(III) INDICATOR REACTION IN ACID SOLUTIONS

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The catalytic titration method was first described by Yatsimirskii and Fedorova [1]. They titrated silver(I) with iodide and detected the end-point by the application of iodide-catalysed cerium(IV)-arsenic(III) indicator reaction, while the change of the indicator substance (cerium(IV)) concentration was followed photometrically.

In our earlier paper [2] a new catalytic-potentiometric titration method for the determination of silver (I) by the application of the iodide-catalysed manganese(IV)-arsenic(III) indicator reaction in the presence of sulphuric acid, was developed.

The results of our preliminary investigations in this work have justified the study of conditions for the application of the iodide-catalysed manganese(IV)-arsenic(III) indicator reaction for the catalytic titrations of silver(I) in the presence of sulphuric acid. The effect of sulphuric acid and of concentrations of some anions (ClO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, SCN<sup>-</sup>), of the molar ratio of manganese(IV) to arsenic(III), respectively, in the titrated solution, as well as the effect of the titrand temperature on the conditions for the determination in solutions of various silver(I) concentrations, was investigated. The error in the determination of 0.5 µg/cm<sup>3</sup> silver was less than ±2%, and the reproducibility of the method is good.

[1] K. B. Yatsimirskii, T. I. Fedorova, *Doklady Akademii Nauk SSSR*, 1962, 43, 43

[2] T. J. Pastor, N. D. Popović, G. M. Petković, *Magy. Kem. Folyoirat*, 1996, 102, 498