

A Comparison of Argentometric Titration and Spectrophotometric Determination of Chloride Concentration in Precipitation Samples

Received for publication, March 3, 2005
Accepted, April 4, 2005

CARMEN IACOBAN¹, MATEI MACOVEANU²

¹ Forest Research Station, Calea Bucovinei 73 bis, 725100 Campulung Moldovenesc, Romania

² "Gh.Asachi" Technical University, Faculty of Industrial Chemistry, Department of Environmental Engineering, Bd. D Mangeron 71 A, 6600 Iasi, Romania

Abstract

The concentration of chloride was determined in parallel for a series of 14 precipitation samples, by argentometric titration (Mohr method) at the laboratory of the Environmental Protection Agency Suceava and by spectrophotometric mercury thiocyanate-iron method at the Forest Research Station Campulung Moldovenesc. The purpose was to permit the comparison of the chloride deposition obtained in time by different laboratories that had used the two methods for chloride determination in precipitation samples. The results demonstrate that the Mohr method chloride concentrations are approximately two times more elevated than those determined by spectrophotometry.

Keywords: chloride concentration, titration, spectrophotometry

Introduction

The importance of chloride determination has been realized for well over a century, with many variations and changes being made to the techniques, in order to improve the detectability and selectivity of the methods. Research into the analysis of chloride was conducted by Gay-Lussac (1832), Level (1853), Mohr (1856) and Volhard (1874) and their findings have proven to be the basis of the methods which are still in common use today:

The most used methods for the determination of chloride concentration in water are:

- Mohr method, consisting in titration of chloride with a solution of silver nitrate in excess, detectable in presence of potassium chromate as indicator. The method is applied in a neutral medium [1]. Concentration range: more than 30 mg/l;
- Charpentier-Volhard method, consisting in precipitation of chloride with an excess of silver nitrate in presence of nitric acid and titration of this excess with a standard solution of ammonium thiocyanate [1]. The method is used when phosphates are present in the sample, in the range up to 30 mg Cl⁻/l;
- turbidimetric method, also based on the reaction of chloride with silver ions and measurement of the turbidity caused by silver chloride precipitation [2]. Concentration range 2-400 mg Cl⁻/l;
- coulometric titration, in which the silver ions are precisely and quantitatively generated at the time of the analysis by passing a constant current between donor electrodes. The end point is detected by the use of sensing electrodes which measure the change in solution conductivity which occurs when excess silver ions are present in solution. Concentration range: more than 10 mg Cl⁻/l [3];
- flow – injection potentiometric titrimetry, which consists in determining the titration end point by the Gran method, using an automatic flow titrator [4];

- indirect method for determining Cl^- , in which AgI was used to precipitate the Cl^- and the excess AgI was converted to the diethyldithiocarbamate chelate and determined spectrophotometrically at 340 nm [5]
- spectrophotometric mercury thiocyanate-iron method, in which the chloride ions substitute the thiocyanate ions in undissociated mercury thiocyanate. The released thiocyanate ions react with ferric ions forming a dark red iron-thiocyanate complex [6]. Concentration range: 0,05-5 mg/l;
- ion chromatography.[7]. Concentration range: 0,02-2 mg Cl^- /l.

In order to assess the levels of mineral ions deposition and their trends for a certain period, it's important to assure the comparability of the results obtained for the studied period. If different methods of analysis had been used, in the same or in different laboratories, the resulting outcomes yielded in parallel by the two methods have to be compared. For France, the atmospheric deposition of the ammonium nitrogen obtained in 1876 – 1907 could be compared to those obtained in 1982 – 1986, because a series of 10 samples were analysed in parallel using both the old and the modern method of determining the ammonium nitrogen in precipitation [8].

For chloride concentrations, comparable results obtained by coulometric titration and potentiometric determination were registered [9].

In this paper, the chloride concentrations for a series of 14 precipitation samples were determined in parallel by means of the Mohr method and by the spectrophotometric mercury thiocyanate-iron method, in order to compare the chloride concentration in precipitation samples and chloride deposition in Romania, obtained starting with the year 1965.

Materials and methods

The 14 samples analysed were snow samples collected:

- on 05.01.1996 in the area of the town Campulung Moldovenesc (samples 17-25, table 1)
- on 04.03.1996 on the transect Iisesti – Gura Humorului – Frasin – Molid – Vama – Prisaca – Campulung.Moldovenesc (samples 55 – 62, table 1).

A comparison of argentometric titration and spectrophotometric determination of chloride concentration in precipitation samples.

The laboratory of the Environmental Protection Agency Suceava used the Mohr method for the analysis of chloride concentrations in precipitation (STAS 3049-1052). For titration, a 0,01 N silver nitrate solution was used, instead the 0,1 N solution recommended by the standard method, in order to improve the precision. The recommended range for this method is more than 30 mg Cl^- /l. Even if the end point of the titration is detected using an electrode, the recommended range is more than 10 mg Cl^- /l.

In the laboratory of the Forest Research Station Campulung Moldovenesc, the spectrophotometric mercury thiocyanate – iron method was used for the determination of chloride concentrations in the 14 samples. Instead of the ferric nitrate solution recommended by EMEP [6], a solution prepared from ferrous ammonium sulfate and nitric acid was used (based on American Society for Testing and Materials -ASTM D512-04). The recommended range for this method is 0,05 – 5 mg Cl^- /l.

Results and discussions

In table 1 the results for the measurements performed in the two laboratories are presented.

Table1. The chloride concentrations in snow samples determined by different methods in two laboratories

Sample number	Sample number in the evidence register of the laboratory FRS Campulung	Concentration of Cl ⁻ (mg/l)	
		Mohr method EPA Suceava	Spectrophotometry FRS Campulung
1	17	4,97	0,67
2	18	6,39	3,09
3	19	3,55	2,33
4	20	2,84	1,55
5	23	2,84	0,75
6	25	2,13	1,33
7	55	4,26	3,50
8	56	3,91	2,35
9	57	4,62	2,52
10	58	4,26	2,38
11	59	2,84	0,57
12	60	2,84	1,84
13	61	3,20	0,35
14	62	4,26	2,14
Mean		3,78	1,81
RSD (%)		30	54

The mean value obtained by spectrophotometry is twice less than the mean measured by titrimetry. This suggested the general tendency to overestimate the results by titrimetry, for low concentrations. In the framework of the AQUACON Project, on the basis of the results of intercalibration exercises to which many European laboratories had participated, also had been noticed the tendency of overestimation the chloride low concentrations by silver nitrate titration [10], [11].

The relative standard deviation was reduced for the determinations made by titrimetry, because of the low precision of the method at low concentrations in chloride. In a study concerning the charges of pollutants ions in snow samples collected in localities from the district of Suceava on 3-4 February 1994 [12], the relative standard deviation was 93-152% for the concentrations of SO₄²⁻, NO₃⁻ and NH₄⁺ and only 57% for chloride, which was analysed by silver nitrate titration. The mean concentration of chloride was 5,41 mg Cl⁻/l. For samples of snow collected on 12-13 February 1994 and presented in the same study, the RSD of SO₄²⁻, NO₃⁻ and NH₄⁺ concentrations varied between 43 and 76% and for chloride was 32%, for a mean value of 4,31 mg Cl⁻/l.

In order to evaluate the comparability of the results obtained by the two methods, the correlation was represented in fig.1.

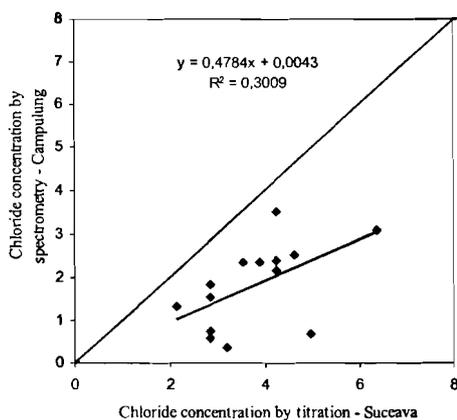


Fig.1 Scatterplot of snow samples chloride concentration as determined by titrimetry (Mohr method) and spectrophotometry (mercury thiocyanate – iron method) used in two different laboratories

A comparison of argentometric titration and spectrophotometric determination of chloride concentration in precipitation samples

The results allow estimating that the chloride concentrations in precipitation samples, for the studied range are generally twice more elevated as determined by titrimetry than those obtained by spectrophotometry. The correlation coefficient of the linear regression is 0,55.

Conclusions

As other publications had mentioned, the Mohr method is not reliable for the determination of low chloride concentrations in precipitation samples. Yet, in Romania, beginning with 1965 [13] results concerning chloride concentration in precipitation determined by Mohr method were reported. This paper established that the conversion of the Mohr method results to those obtained by spectrophotometry can be approximate by dividing them to 2. That offers the possibility to compare the chloride concentrations and deposition obtained in time in Romania.

References

1. RODIER, J., L'analyse de l'eau. Dunod. Orleans:1365 p., 1984
2. MESQUITA, R.B.R., FERNANDES, S.M.V., RANGEL, A.O.S.S., Turbidimetric determination of chloride in different types of water using a single sequential injection analysis system, *J. Environ. Monit.*, 4: (3), 458-461, 2002
3. GENEQ. Biotechnology. Chloride Analyzers, Chloride Analyzer Model 926: http://www.geneq.com/catalog/en/ca_926.html
4. ALMEIDA, C. M. N. V., ARAUJO, M. C. U., LAPA, R. A. S., LIMA, J. L. F. C., REIS, B. F., ZAGATTO, E. A. G., Precipitation titrations using an automatic titrator based on a multicommutated unsegmented flow system, *Analyst (Cambridge, U.K.)*, 125, 333-340, 2000
5. UTSUMI, S., MATSUNO, S., ISOZAKI, A., *Bunseki Kagaku*, 40:(8), 257-262, 1991
6. EMEP, *Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe. Manual for sampling and chemical analysis*,

- EMEP/CCC-Report 1/1995, Norwegian Institute for Air Research, Kjeller, Norway, 4-27-4-28, 1996
7. Determination of Anions in Acid Rain by Ion Chromatography
<http://www1.dionex.com/en-us/webdocs/articles/ic/anion/AU146.pdf>
 8. ULRICH, E., WILLIOT, B., Les depots atmospheriques en France de 1850 à 1990, Office National des Forêts (Eds.), France, 154 p., 1993
 9. CEBRA, C.K., TORNQUIST, S.J., VAP, L.M., DODSON, L.A., A comparison of coulometric titration and potentiometric determination of chloride concentration in rumen fluid, *Veterinary Clinical Pathology*, Vol.30, 4, 211-213, 2001
 10. MOSELLO, R., BIANCHI, M., BRIZZIO, M.C., GEISS, H., LEYENDECKER, W., MARCHETTO, A., REMBGES, D., TARTARI, G.A., MUNTAU, H., AQUACON – MedBas PROJECT Subproject No. 6, Acid rain analysis, Intercomparison 1/98, Results from the laboratories participating in the ICP Forests, Environment Institute, Joint Reseach Centre, Ispra (Italy), 32 p., 1999
 11. MOSELLO, R., TARTARI, G.A., BIANCHI, M., BRIZZIO, M.C., GIULIANO, R., MARCHETTO, A., POLESELLO, S., REMBGES, D., MUNTAU, H., AQUACON – MedBas PROJECT Subproject No. 5, Freshwater analysis, Intercomparison 2000, EUR 20427 EN, European Communities, 114 p., 2002
 12. BARBU, I., DITOIU, V., Cercetări asupra conținutului în ioni poluanți a apelor din precipitații căzute în județul Suceava în perioada 1991- 1994, *Bucovina forestieră*, 2, 37-49, 1995
 13. MAGIRICU, V., Determination of content of Cl⁻ and SO₄²⁻ in precipitation water at Bucarest, in "Collection of papers of the National Meteorological Institut", Bucuresti, 195-201, 1965