



Determination of halides in drinking/waste water by coulometry



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TITRIMETRIC METHODS ARE widely used in research and industry. One of the most interesting titrimetric method is the coulometric titration, a term derived from coulombs. Using coulometry at controlled or constant current, the range of substances that can be determined may be extended considerably, and includes those which don't react quantitatively at an electrode. Constant current coulometry is employed to generate a reagent electrochemically under conditions of constant current, which reacts stoichiometrically with the substance to be determined (Kirowa, 1998, Tzur, 1997).

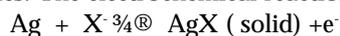
Coulometric analysis is an application of Faraday's first law of electrolysis, which may be expressed in the form that the extent of chemical reaction at an electrode is directly proportional to the quantity of electricity passing through the electrode. The present work is focused on the analysis of halide ions (Cl⁻, Br⁻ and I⁻) in water samples. All life on earth depends on water. The form in which the chemical compound H₂O manifests itself is variously modified by its physical properties, its capacity to dissolve solid, liquid and gaseous substances and hence by its secondary chemical action and the fact that water provides a habitat for a wide variety of organisms. These characteristics of water are an important factor to man, who uses the water for drinking or technical purposes. These anions from different sources can enter easily into water system and then they take their way directly into the human body. The intake of toxic as well as essential elements through water and other food items like vegetables, milk, wheat flour etc. is significant (Viqar, et. al. 1992, 1994.) The abundance or deficiency of these anions results in abnormal metabolic functions. Chloride ions play important role in water balance and osmotic pressure regulations in kidney. The body contains 15-20 mg of iodine which is mainly concentrated in thyroid gland and is used in the formation of thyroid hormone. The suggested intake of I⁻ or I₂ is 100-200 mg/day. The deficiency of I results generally to the enlargement of thyroid gland (goiter formation). The conc. of Br⁻ at very trace level is toxic, so the conc. of these anions must be checked and monitored (Khurshid, 1983)

Method

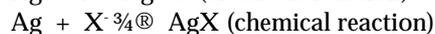
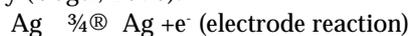
The model 179-digital coulometer which is a plug in module designed with the model 173 Galvanostat / Potentiostat is used for making coulometric measurements at controlled current. The model 173/179 system from Princeton Applied Research U.S.A. is highly versatile, it is easy to operate, and is thus as well suited to routine

measurements. Automatic subtraction of any background current is provided by means of a background current adjustment.

For analysis purposes, a cell having two compartments separated with sintered glass disc is used. A pure silver wire, gauze or foil of large surface area (10-20 Cm²) as generator anode, A platinum wire helix is used as the cathode and the saturated calomel electrode as the reference electrode (Lingane, 1958). The coulometric titration of chloride, bromide and iodide with electrolytically generated Silver(I) is an accurate and precise method. Different supporting electrolytes like for chloride (0.04M sodium nitrate + 0.05M perchloric acid in 80 volume percent ethanol water) Br⁻ (0.50 M HClO₄ + 2.0 M Potassium nitrate) and I⁻ ((0.095M HClO₄+0.409M KNO₃), were used for these studies. The electrochemical reaction is:-



(Where X⁻ may be Cl⁻, Br⁻ and I⁻) supports the cell current during the early stages of this titrations, i.e.; when the limiting current for X⁻ is greater than the cell current. The reaction mechanism could be explained in the following way (Vogel, 1978).



The coulometric end-point can be detected quite satisfactorily in these titrations using different end point detection methods like use of chemical indicators, potentiometric or amperometric procedures. (Vogel, 1978)).

Results and discussions

Automatic titrations are essential in modern analytical chemistry. Coulometric titrations dealing mainly with the processes at the generating electrodes were extensively studied in the past. Today, as new methods for the end point detection and computerised instrumentations are developed, there is a need to re-establish and optimize these methods. For the present studies main emphasis was given to the optimization of coulometric titration. Constant current coulometry was carried out on 0.00ml -10.0ml solutions of standard HCl (5.206x 10⁻⁴M) KBr 9.794x10⁻⁴M and KI 9.919x10⁻⁴ M. The results are presented in tables 1-3. It is clear from tables that the percentage error for halide determinations decreases in the following order Cl⁻ > Br⁻ > I⁻. Probably, it is due to the gradual increase in atomic weight from Chloride to Iodide. Table-4 gives the details about the instrumentation for chloride, bromide and iodide by coulometry at constant current.

After optimization the procedure was used for the analysis of several drinking water samples from Rawalpindi-Islamabad area. In Rawalpindi-Islamabad areas surface as well as ground waters are used for drinking purposes. The tolerable limit of Cl⁻ is 200 ppm, above this limit abnormal symptoms may appear. Cl⁻ ions are also involved in maintaining the acid base balance of the blood by the action of Cl⁻ shift and in the production of HCl. The suggested intake of Iodide or iodine is 100-200 mg/day. As in this area of Rawalpindi-Islamabad the enlargement of thyroid gland which is commonly observed is mostly encountered to drinking water, being the main constituent of our food. The significance of bromide is not commonly known but it is very toxic even at trace level. the concentration of bromide in water samples shows the accumulation of industrial effluents, polymers as well as plastics.

Many samples of drinking water and waste water were analysed from Rawalpindi-Islamabad area. Some of the results are given in (Table-5). Samples R₁-R₅ are drinking water samples collected from Rawalpindi and samples I₁-I₅ are drinking water samples from Islamabad area. Generally the levels of chloride and bromide are slightly higher in samples from Rawalpindi area as compared to Islamabad, but all the values are well below limits. Values of Iodide are more or less similar with slight variations. These are also below limits. Samples P₁ - P₄ were collected from different ponds in Islamabad. where natural and waste water is accumulated. In these samples values of halides particularly of chloride are relatively higher than the drinking water

samples, but these values are also well below limits. It shows that in water samples from Rawalpindi-Islamabad area levels of halides are generally low.

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Table 1.

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Table 2.

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Table 3.

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Table 4.

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Table 5.

