# Automated Wet Chemical Microcoulometric Analyzer for Chloride Ion[1]

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An automated system for the rapid, reproducible analysis of chloride ion in aqueous samples by a combination of Technicon[2] AutoAnalyzer and Dohrmann[3] microcoulometric titration modules is described. This chloride analyzer, designed especially for the chloride ion derivable by various means from organochlorine pesticides, should be broadly applicable to many other analytical situations for chloride ion requiring high precision and rapid analysis. End chloride detection is by the well-known Dohrmann microcoulometric titration system (CHALLACOMBE and McNULTY 1964); use of this detector in a continuous wet analytical method is apparently new.

## PROCEDURE

### Equipment

The chloride analyzer is set up as diagrammed in Fig. 1 and as described below, using the following equipment:

1 - Technicon sampler II module with 30/hr, 1:6 cam (20 sec sampling:100 sec wash).
1 - Technicon proportioning pump I module.
1 - Dohrmann T-300S titration cell.
1 - Dohrmann C-200A microcoulometer and matched 1-mV recorder with Disc integrator.

Microcoulometer operating mode: bias, 250 mV; gain, "Hi"; high gain, setting 50 to 75; range-ohms, set as required for detectability of sample; cell cap set with "green" sensor electrode about 15° counterclockwise off center of "white" reference arm fritted-glass disc; stirrer set at low speed. Make final adjustment on the last four settings individually (including stirrer) for maximum peak response with minimum tailing or overshoot.

Alternatively, if only early model Dohrmann equipment is available, use the following equipment and instructions:

1 - Technicon sampler II module with 30/hr, 1:1 cam (1 min sampling:1 min wash).
1 - Technicon proportioning pump I module.

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[1] Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, CA, Apr. 2, 1968.
[2] Technicon Instruments Corp., Tarrytown, N.Y. 10591.
[3] Dohrmann Div., Envirotech Corp., Mountain View, CA 94040.

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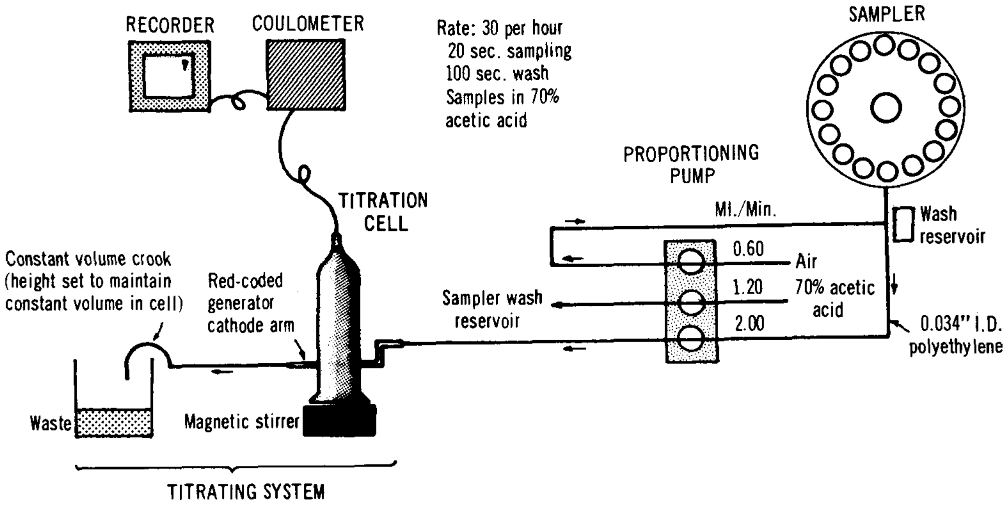

FIG. 1. Flow diagram of automated chloride analyzer. Sample line connection to cell is by means of Tygon transmission tubing to a Technicon plastic nipple force-fitted into a 1-in. length of 2-mm capillary glass tubing with ball joint to mate the normal spherical joint of the cell.

1 - Dohrmann T-200S titration cell.
1 - Dohrmann C-100 coulometer and matched 1-mV recorder with Disc integrator.

Coulometer operating mode: bias, 250 mV; recorder time constant, 2; damping, 3; range-ohms, set as required for detectability of sample; cell cap and stirring rate adjusted for maximum peak response with minimum tailing or overshoot.

Operation

Samples must be introduced to the chloride analyzer in 70% acetic acid, the carrier liquid required by the titration cell. As the sampler module operates, either a sample in 70% acetic acid or a wash stream of 70% acetic acid is pumped by the proportioning pump into the inlet of the titration cell. This pumped liquid stream is continuously segmented with air for best pumping characteristics. The microcoulometric titration system furnishes continuous signal to the recorder for readout. The flexible siphon tubing fitted to the titration cell maintains constant volume: the glass crook at the end of this tubing is adjusted in height until gravity flow output through the open stopcock on the cathode side arm (McNULTY 1966) balances input from pump to cell. More recently it has been found that less signal noise is produced if this constant-volume technique is replaced by the following: aspirate excess electrolyte out through a long drawn-out dropping pipet inserted from the top opening in the cell cap; the tip of the pipet is adjusted to the desired level and the other end is connected to a vacuum waste trap.

## RESULTS AND DISCUSSION

Fig. 2 is a representative recording obtained from sampling (30/hr) several replicates of a test solution of sodium chloride in 70% acetic acid. Note the precision obtained among the integrated peak areas, recorded with the microcoulometer operating at only 10 ohms (maximum response setting is 999 ohms; the full range is not usable, however, due to excessive signal noise). Calculations from the Dohrmann coulometric equation, which in this case reduces to peak area times 0.442, indicate a mean operational efficiency of 97±1% for this series of five replicates.

Fig. 3 shows almost equally good reproducibility among replicated samples even when a low-concentration sample follows one of high concentration, with a mean operational efficiency of 96±3%.

The system from which these data were obtained is convenient and simple to set up and operate. Suggested usage of the system is for organochlorine compounds which have been combusted in a Schöniger flask (BONTOYAN 1964, LISK 1962) or in a furnace (AGAZZI *et al*. 1953) with combusted products collected in chloride-free distilled water. Glacial acetic acid must then be

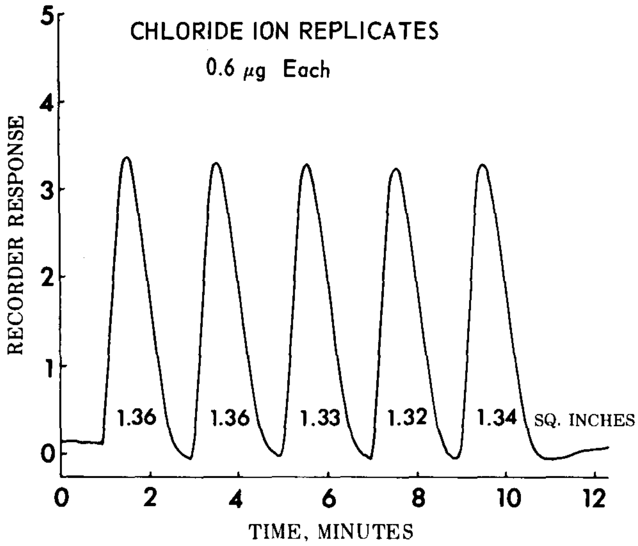

FIG. 2. Chart recording of replicate standards from chloride analyzer according to Fig. 1 with the late model Dohrmann equipment: 30 samples/hr, microcoulometer settings at 10 ohms and 50 high gain. The sample pump tube, as segmented with air, pumps 0.43 ml for each 20-sec sampling period. Standard was 1.42 μg $Cl^-$ (as NaCl)/ml in 70% acetic acid. Zero time is start of sampling of first sample.

added to each sample to give a final 70% acetic acid solution[4/] for submission to the chloride analyzer. Replicated furnace combusted samples, consisting of μg to mg amounts of dieldrin, yielded peaks no different from those in Figs. 2 and 3 with 90±4% recoveries of chloride ion.

The system now employs the Dohrmann model C-200A microcoulometer and T-300 titration cell; however, the early models C-100 coulometer and T-200 titration cell were originally used but the later equipment is more responsive and is thus preferred.

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[4/] This has later been done automatically by slight modification of the system shown in Fig. 1 by pumping glacial acetic acid through a 0.073 in. i.d. (1.44 ml/min) Acidflex pump tubing and with a mixing coil to mix the aqueous sample with the glacial acetic acid.

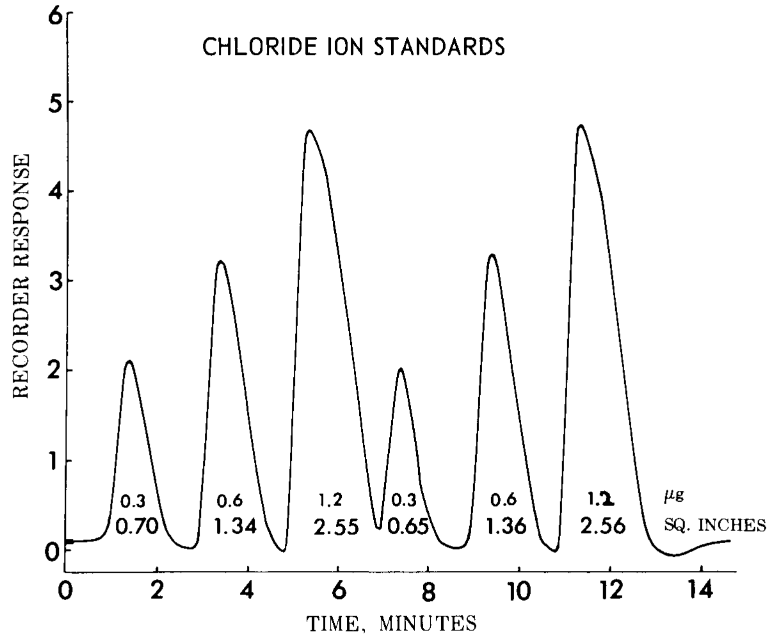

FIG. 3. Chart recording of replicated standard dilution series from chloride analyzer with conditions as in Fig. 2. Standards sampled were 0.71, 1.42, and 2.84 μg $Cl^-$ (as NaCl)/ml in 70% acetic acid.

This chloride analyzer was first presented (OTT and GUNTHER 1968) in connection with a system to automatically degrade organochlorine compounds to liberate chloride ions by means of sodium biphenyl reagent. However, problems of working with this relatively unstable reagent in a routine manner have essentially halted further development of this part of a total system. Another abandoned approach, which met with partial success, included direct combustion of the sample in hexane solution pumped into a hydrogen flame with aspiration of combusted products into a pumped stream of water as trapping liquid for dilution with acetic acid and delivery to the microcoulometric titration cell. Microgram amounts of DDT, with relatively poor recoveries, were detectable but considerably larger amounts of dieldrin were not detectable; presumably the necessary hexane cooled the hydrogen flame so that combustion of solute was incomplete and also dependent upon the structure of the solute. A better automated system for dechlorinating organochlorine compounds needs to be developed.

This detailed description of the chloride analyzer makes it ready for immediate application for low-level aqueous chloride ion provided that interferences such as bromide, iodide, and fluoride ions are not present. Following high temperature oxidative ($O_2$) or reductive ($H_2$) decomposition of organochlorine compounds with collection of released chloride ion, it presently will provide a precise and rapid automated end detection system for nonspecific screening for these compounds in a large number of substrates at ppm and sub-ppm levels.

## ACKNOWLEDGMENTS

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