RESIDUE ANALYSIS

Direct Potentiometric Method for Chloride Ion Applied to Residues of Chlorinated Insecticides

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The quantitative determination of chlorinated-insecticide residues in treated foodstuffs by total chlorine methods is expedited and simplified by the exploitation of an unusually sensitive direct potentiometric method for chloride ion. This method uses a pH meter and a silver–silver chloride vs. calomel electrode system, and responds reproducibly to as little as 0.02 p.p.m. of chloride ion. With the equipment and procedures recommended, the useful range, without concentration or dilution stages, appears to be from 0.02 p.p.m. to 10,000 p.p.m.

PERSISTING RESIDUES OF AN organic insecticide applied during or after the growing stages to foodstuffs for human or animal consumption must be evaluated both toxicologically and analytically before the insecticide can be registered and licensed for general sale within the United States. In the absence of more specific and applicable analytical methods, some of the total chlorine methods (*1, 6, 7*) are considered to be capable of providing useful residue information when the insecticide contains organically bound chlorine. When insecticide-containing soil, plant, and animal extractives are involved, precise determinations of the ultimately released chloride ion are often difficult and questionable because of interfering accessory substances present (*6*). Frequently, also the available methods for determining chloride ion from soil, plant, and animal extractives are not sufficiently sensitive to meet anticipated Federal tolerance requirements, as with some types of potentiometric tritrations. Amperometric titrations are usually more sensitive but complicated enough to cause losses or contamination in routine applications.

Of the approximately 80 insecticides in current commercial use, 40 contain organically bound chlorine. Thus, methods for determining magnitudes and locales of maximal residues of these materials via their chlorine contents are important.

The present method [briefly mentioned by Gunther and Blinn (*6*)] for the simple yet accurate determination of chloride ion was developed from that of Furman (*4*), Furman and Low (*5*), and Blaedel *et al.* (*2*). It meets the exacting needs of routine microanalyses in conjunction with the combustion (*1, 6, 7*) of extractives from plant parts and soils treated with chlorinated insecticides. An additional advantage of this procedure is its applicability to measurement of chloride ion at concentrations of the order of, or considerably below, that arising from the silver chloride itself.

Previously, reproducible direct potentiometry has usually been applied to solutions of relatively high chloride concentrations with a concentration cell system containing two silver–silver chloride electrodes (*2, 5, 8*)—for example, Furman and Low (*5*) do not report detection below 0.35 p.p.m. chloride ion, but Blaedel *et al.* (*2*) report in summary a limiting chloride ion concentration of 0.07 p.p.m. The present method employs a silver–silver chloride vs. calomel system, which is more convenient than a concentration cell for a control method, because standard chloride solutions are necessary only for the initial calibration of a potentiometer. Chanin (*3*) has just reported use of the same electrode system in chloride determinations, but he achieves a useful range of from 4 to about 100 p.p.m. and does not recognize the important temperature dependency of the system.

In the present method optimum results are obtained at 10 p.p.m. chloride (2.82 × 10^{-4} equivalent/liter) with a standard deviation of less than 0.1 p.p.m. At concentrations from 0.02 to 1.00 p.p.m., results are reproducible to 0.02 p.p.m. Direct measurements have also been made on solutions containing as high as 10,000 p.p.m. chloride ion.

Table I. Calibration for Low Concentration Range

(T = 40.0° C.; Ksp = $10^{-9.24}$)

[Cl⁻]$_a$, P.P.M.	Helipot Reading
1.00	630
0.50	679
0.10	723
0.01	735
0.00	739

Description of Apparatus

Calomel Electrode A miniature calomel electrode (Beckman No. 270) with an asbestos fiber bridge–solution retainer was especially selected for low leak rate characteristics.

Silver–Silver Chloride Electrode A miniature silver billet electrode (Beckman No. X559-190A, style 270, silver billet) was cleaned with a mild abrasive and a dilute detergent solution, then coated electrolytically in a saturated potassium chloride solution, using two 1.5-volt dry cells in series. The current was reversed at 5-second intervals between the billet

Table II. Calibration for Intermediate Concentration Range

$$(T = 40.0° \text{ C.}; \quad Ksp = 10^{-9.24})$$

| [Cl⁻]a, Eq./Liter × 10⁴	[Cl⁻]$_{tot}$., Eq./Liter × 10⁴	—Log [Cl⁻]$_{tot.}$	E.m.f., Mv.[a]
0.06[b]	0.27	4.569	−41.4
0.14	0.32	4.495	−37.8
0.28[c]	0.42	4.377	−29.4
0.42	0.53	4.276	−22.0
0.56	0.65	4.187	−12.8
1.13	1.18	3.928	+11.0
1.69	1.73	3.762	32.4
2.82	2.85	3.545	59.4
5.64	5.66	3.247	98.2
8.46	8.47	3.072	121.2
14.11	14.12	2.850	149.8
25.39	25.39	2.596	184.0

[a] These results were obtained from prototype Beckman GS pH meter in which pH slide wire was replaced by fixed resistance. When the e.m.f. was outside the range covered by the helipot, the calibrated #1 balance adjustment was used for extending scale. Apparent negative e.m.f. values merely indicate that measurements were made below lower limit of helipot.

[b] 0.2 p.p.m.

[c] 1 p.p.m.

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electrode and pure silver wire until a homogeneous purple coating of silver chloride would appear rapidly on the silver billet. Before use, the coated billet was aged for 1 hour in acidified water at the pH to be used for subsequent e.m.f. measurements. One coating was sufficient for several hundred measurements if the electrode was not allowed to dry during use. It could be conveniently stored in a saturated solution of potassium chloride at room temperatures, but is poisoned by bromide ion.

Figure 1. Reflux system for temperature control

To reflux condenser

12 mm. I.D. U-tube for electrodes and sample

5 cm.
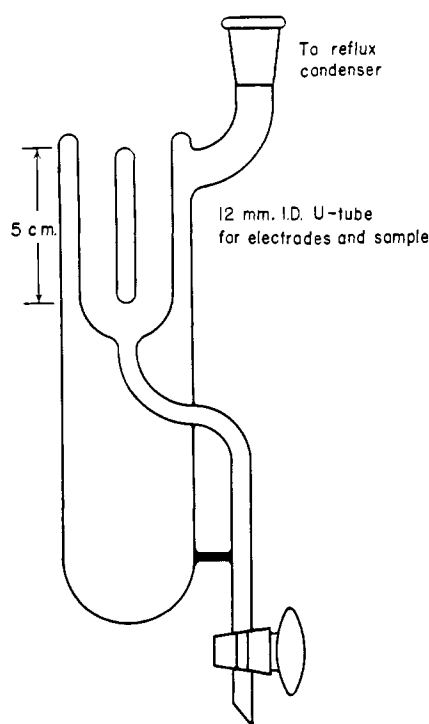
Sample and Electrode Holders Because of the millivolt sensitivity in this system it was necessary to maintain constant temperature in the sample container to avoid the effects of the various thermodynamic temperature coefficients of e.m.f. which are characteristic of electrochemical measurements. The temperature was controlled by using either a reflux system, Figure 1, or a circulating water system, Figure 2. By fabricating the electrode-holding tubes so that only about 5-mm. distance remained between the bottom of the electrodes and the bottom of the U-tube, the amount of sample needed for a single measurement can be held to less than 3 ml.

Convenient liquids for refluxing in the temperature control system of Figure 1 were methylene chloride, boiling point 40° C., or methyl formate, boiling point 32° C. With either system, prewarming the sample in an incubator or water bath facilitated measurement.

Potentiometer A prototype Beckman model GS pH meter was used for the measurement of e.m.f., but a Beckman model H-2 line-operated pH meter was found useful within the range 10 to 1000 p.p m. chloride ion, with about ±15% precision. In the model GS instrument the zero adjusting potentiometer had been replaced by a 10-turn helical potentiometer equipped with a multi-turn indicating dial knob of 1000 divisions. A differential voltage of 100 millivolts could be read with an average reading error of ¹/₄ division (= 0.025 mv.) on the helical potentiometer. (The Beckman model GS meter available commercially reads 200 millivolts across this potentiometer, hence has twice the differential range.) The

standard pH slide wire was used as a "coarse" adjustment knob to establish the potential region to be differentially measured by calibrating the system with the potential developed, when the electrodes were immersed in a standard solution of known chloride content. Two
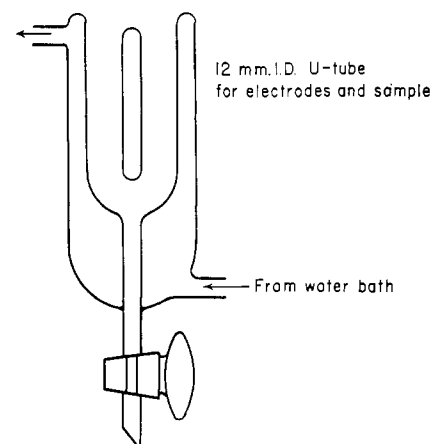

12 mm. I.D. U-tube for electrodes and sample

From water bath

Figure 2. Water circulating system for temperature control

different settings using one standard chloride solution (2.82 × 10⁻⁴ equivalent/liter, 10 p.p.m.) were used to cover the concentration range from 0.02 to 100 p.p.m. The instrumental knob settings were reproducible to ±1% on a day-to-day basis once the calibration scale had been established.

Procedure for Routine Measurements

Precautions The electrode system was subject to interferences by those anions which complex or precipitate silver ions in acid solution more efficiently than chloride ions. If the con-

Table III. Calibration for High Concentration Range

(T = 40.0° C.; helipot set at 500, readings taken with pH dial)

[Cl⁻]$_{tot.}$, Eq./Liter	—Log [Cl⁻]$_{tot.}$	pH Dial Reading
0.000282[a]	3.545	3.89
0.001410	2.850	4.57
0.00282	2.545	4.87
0.00564	2.248	5.19
0.01128	1.948	5.48
0.01692	1.772	5.64
0.0225	1.647	5.77
0.0282	1.545	5.88
0.0564	1.248	6.17
0.1410	0.851	6.57
0.254[b]	0.595	6.79

[a] 10 p.p.m.

[b] 9000 p.p.m.

centration of these extraneous ions was great enough to react metathetically with the solid silver chloride coating, secondary e.m.f.'s resulted. A common interfering ion was carbonate ion, especially because sodium carbonate solutions are used to collect chloride in a combustion train (1, 6, 7). The action of this ion was suppressed by making all measurements in solutions acidified with chloride-free nitric acid at the rate of 1.0 ml. of 16N acid per 50 ml. of final solution.

In order to maintain practically constant ionic strength, all standard solutions were prepared in a carbonate solution of the same concentration as that used in the absorbers of the combustion train—namely, 20 ml. of 0.2% sodium carbonate solution diluted to a final volume of 50 ml.

Before measurement, the sample solutions were warmed for 30 minutes at the temperature of the electrode and sample holder. This eliminated excessive time for temperature equilibration in the system.

Operational Steps for E.m.f. Measurement Procedure Set the instrument range switch to pH, the sensitivity switch to B, and the operating switch to "1." After sufficient warm-up time, or about 10 minutes, balance the instrument circuit according to the manufacturer's instructions.

Add prepared standard chloride solution, containing 2.82 × 10⁻⁴ equivalent/liter, to the U-tube (Figure 1 or 2), and insert the electrodes.

Set the helical potentiometer scale at about 100 units (one full turn) from the lower limit, then, while depressing the push button, turn the pH dial to balance the galvanometer needle. Accurately

note and record the position of the pH dial for future reference.

Discussion of Procedure This procedure establishes one point on the calibration curve for the measurement of chloride concentrations from 10 p.p.m. down to 0.02 p.p.m. Other points are obtained by measuring several chloride standards of decreasing concentration using only the helical potentiometer scale. The pH dial setting must not be changed during measurements in a given concentration range.

The potential is read on consecutive fresh portions of each solution until the readings are consistent to ±0.2 milli-

volt. An arbitrary equilibration time of 30 seconds is allowed between introduction of the sample and reading the potential.

By repeating the last two steps with the same standard solution (2.82 × 10⁻⁴ equivalent/liter), but with the initial helical potentiometer setting about 100 units from the upper end of the scale, the calibration curve can be extended to chloride concentrations from 10 to 100 p.p.m. With the same procedure, but with a standard solution containing 1000 p.p.m. of chloride ion, the range can be extended from 100 to 10,000 p.p.m.

Table IV. Effect of Temperature on E.m.f.

[Cl⁻]$_a$ = 2.82 × 10⁻⁴N

| T, ° C.	E.m.f., Mv.
40	31
31	50
16	79

Calibration Curves

According to the Nernst equation, a plot of log a $_{Cl⁻}$ vs. e.m.f. is linear.

$$E = E° - 0.0591 \log a_{Cl⁻} \simeq$$
$$E° - 0.0591 \log [Cl⁻] \quad (1)$$

In order to maintain this relationship in this series of measurements, the concentration value for chloride had to include a total of the initial chloride present plus that arising through dissolution of silver chloride from the surface of the electrode.

Figure 3. Typical calibration curve for Beckman model GS pH meter at high chloride ion concentrations
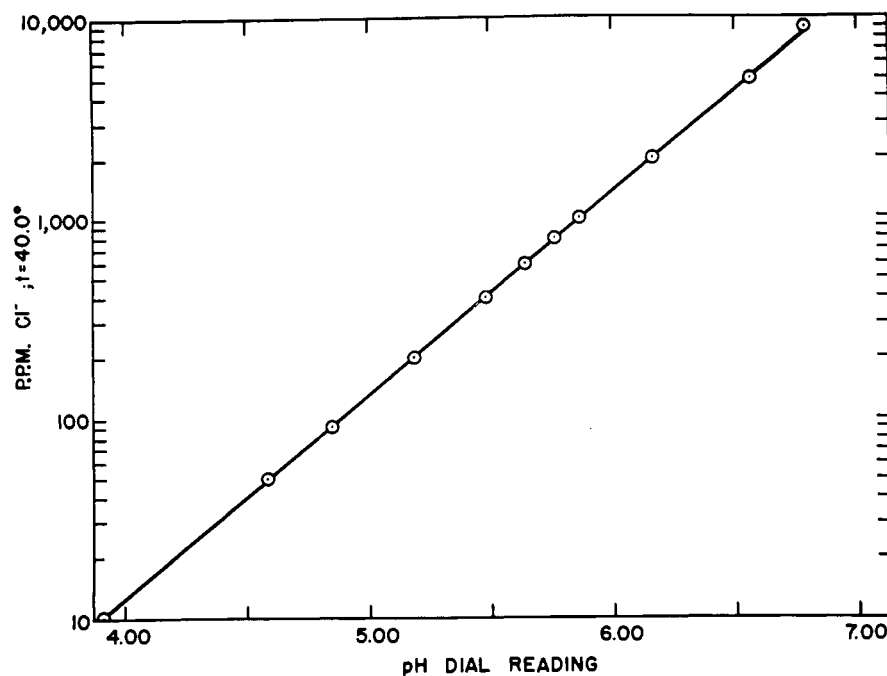
$$[Cl^-]_{tot.} = [Cl^-]_a + [Cl^-]_b \qquad (2)$$

where, $[Cl^-]_{tot.}$ = total chloride, equivalent/liter

$[Cl^-]_a$ = chloride initially present, equivalent/liter

$[Cl^-]_b$ = chloride from electrode, equivalent/liter

The solubility product constant, Ksp, is given by

$$[Ag^+]([Cl^-]_a + [Cl^-]_b) = Ksp \quad or \quad (3)$$

$$[Cl^-]_b([Cl^-]_a + [Cl^-]_b) = Ksp$$

Using equations 2 and 3, the total concentration of chloride ion can be calculated as a function of the initial chloride concentration and the solubility product constant, as

$$[Cl^-]_{tot.} =$$

$$\frac{[Cl^-]_a + \sqrt{([Cl^-]_a)^2 + 4Ksp}}{2} \quad (4)$$

The solubility product constant, Ksp, was estimated graphically by the valid assumption of a linear plot of log Ksp vs. T from about 15° to about 45° C. For routine application at these ordinary temperatures, Ksp values for silver chloride in the absence of other ions were found to be sufficiently accurate.

In equation 4, when $[Cl^-]_a$ is greater than about 0.0015 equivalent/liter, the value 4 Ksp (solubility product constant) becomes insignificant, and the total chloride is then equal to the initial chloride.

Typical calibration measurements for low, intermediate, and high ranges are reproduced in Tables I, II, and III. These calibration measurements were made with the Beckman Model GS pH meter. The precision attainable is clearly shown in the typical calibration curve for the high ranges, Figure 3. Calibration data and curves will differ with different potentiometers and with different calomel electrodes.

Discussion

This variation of direct potentiometric methods for determining chloride is especially suitable for routine application because the necessity for evaporative concentration of samples will rarely be met; this method appears to be useful over a 500,000-fold change in chloride concentration. Since a finite amount of chloride, equal to $(Ksp)^{1/2}$ silver chloride, is always present even though none is present in the original sample, there is no theoretical lower limit on the chloride necessary for e.m.f. measurements. Practical limits are imposed only by potentiometric sensitivity and by variations in Ksp due to deviations of temperature and ionic strength (5).

In a $2.82 \times 10^{-4}N$ solution of chloride ion, Δ e.m.f./Δ T is equal to 1.9 millivolts per degree, affording an error of about 10% per degree (Table IV). However, with temperature control the average deviation of e.m.f. for 30 samples at this concentration was 0.5% and the maximum deviation was 1.0%. These comparisons were made over a period of several months with different operators, electrodes, and standard solutions. Standard percentage deviations for various ranges of chloride concentrations are collated in Table V.

Table V. Standard Deviations in E.m.f. for Various Chloride Concentrations

(T = 40° C.)

$[Cl^-]_a$, Eq./Liter $\times 10^4$	Standard Deviation, %
0.03	10
0.3	2
3.0	0.3
30.0	1

As a practical check of the method, several pairs of typical control samples were processed (6), and burned in the usual manner (1, 6, 7). One sample from each of these pairs was fortified with a known amount of a chlorine-containing insecticide (purified dieldrin, 56% chlorine). After combustion, the amount of apparent fortification was calculated by the increase in chloride concentration over that found in the companion control sample. Typical results are presented in Table VI.

This method has been applied routinely to chloride determinations in approximately 2000 soil and citrus fruit samples before and after treatment in the field with aldrin, Aramite, benzene hexachloride (BHC), chlordan, chlorobenzilate, p-chlorophenyl-p-chlorobenzene sulfonate, dichlorodiphenyltri-chloroethane (DDT), dieldrin, endrin, heptachlor, isodrin, lindane, methoxychlor, sulphenone, and toxaphene. These several insecticides and acaricides vary in content of organically bound chlorine from about 10% for Aramite to about 70% for the benzene hexachloride compounds. Each of them was statistically determinable at about the 0.1 p.p.m. level with samples replicated from 4 to 6 times and after suitable cleanup to remove inorganic chloride prior to combustion. For example, analyses of 38 control samples of orange peel and juice extractives treated with buffered permanganate in acetone prior to combustion afforded an apparent background content of dieldrin (56% chlorine) of 0.19 ± 0.04 p.p.m. for the peel and 0.05 ± 0.01 p.p.m. for the juice. Manuscripts detailing these applications of this versatile analytical technique are in preparation.

Literature Cited

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Table VI. Determination of Organically Bound Chlorine in Dieldrin Fortified Combustion Samples

Sample[a]	Fortification with Purified Dieldrin			
	Amount added, mg.		Amount found, mg.	
Orange peel extractives	1.08	1.09	1.08	1.10
(1 lb. of peel)	0.54	0.54	0.53	0.53
Orange juice extractives	1.08	1.12	1.10	1.10
(1 gal. of juice)	0.54	0.55	0.54	0.54
Soil extractives	1.08	1.09	1.11	1.08
(1 kg. of soil)	0.54	0.58	0.55	0.54
White oil	1.08	1.09	1.09	1.08
(0.2 ml.)	0.35	0.35	0.34	0.35

[a] Large laboratory subsamples are still required to ensure adequate representation of field sample. In many instances, this method will permit the use of much smaller subsamples.