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# Assessment of Some Aqueous Residual Chlorine Measurements

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Application of chlorine as a water disinfectant is known to result in the formation of volatile and non-volatile chlorinated materials from organics already present in the water (OLIVER 1978). Chlorine dosage and demand, total organic carbon levels, and temperature have been related (H.W.C. 1977, YOUNG & SINGER 1979) to trihalomethane levels in potable water supplies.

An extensive monitoring study, encompassing three water treatment systems, required determination of the relationship between several water parameters including residual chlorine levels. Residual chlorine measurement methods, as applied by collaborating laboratories, were compared. Also, residual chlorine values from stored water samples were assessed for use in correlation studies.

## EXPERIMENTAL

Materials. Water, free of chlorine residual, was prepared, as needed, by boiling purified (Super-Q) water in an open glass container until 75% of the original volume remained. Reagents for the analytical methods were prepared as described elsewhere (A.P.H.A. 1975, ORION 1976). Aqueous sodium hypochlorite (6.1%, G.T. Baker Chemical Co.) and chlorine free water were mixed in 10 L polyethylene carboys to obtain bulk solutions containing approximately 0.8 and 1.8 ppm total available residual chlorine (TARC) on the day of analyses.

Amber, glass bottles (125 and 500 mL capacities) were heated at 400°C for 2 hr, cooled, and sealed with Teflon disks and screw caps.

Analytical methods. Laboratories A and B (treatment plants 1 and 2) utilized the amperometric titration (AT) method (A.P.H.A. 1975, method 409C) for free (FARC) and total available residual chlorine determinations. Laboratory C utilized the residual chlorine electrode (EL) method (ORION 1976) for TARC determinations and the DPD ferrous titrimetric (DPD) method (A.P.H.A. 1975, method 409E) for FARC and TARC determinations. Samples for analysis by the AT method were collected in 500 mL capacity, amber, glass bottles and samples for the EL and DPD methods were collected in 125 mL capacity bottles. Blank determinations of chlorine free water were used to correct TARC and FARC values.

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Methods evaluation. Chlorine free water, 0.8 ppm, and 1.8 ppm (TARC) chlorine water solutions were quickly distributed and sealed into amber, glass, bottles. Filter effluent, plant effluent, and tap water samples were similarly collected from treatment system 1. The filled bottles were distributed between collaborating laboratories A, B, and C and the contents were analyzed at predetermined time intervals. Triplicate determinations (one determination per bottle) of each water type and for each storage time were made by each analytical method for relative standard deviation (RSD) calculations. The mean values for triplicate determinations by each method were used for overall RSD calculations. Regression curves for plotting the change of RC with storage time were determined by the method of least squares and analysis of variance was used to compare values describing the curves.

Monitoring study. Filter effluent, plant effluent, and tap water samples from three treatment plants (1, 2 and 3) were collected in duplicate for TARC and FARC determinations on 11 days over a 10 month period and as part of an extensive, multiparameter, water quality study. Samples were analyzed at laboratories A (method AT-A) and C (method EL-C) after known (± 15 min) storage periods. Correlation coefficients were calculated from, and analysis of variance was applied to, daily method mean TARC values for each water type.

## RESULTS AND DISCUSSION

Solutions of sodium hypochlorite were used for comparison of the AT, EL, and DPD methods, since residual chlorine (TARC and FARC) levels in the solutions were stable after several hours of storage. In general, the AT method provided better precision than the other two methods (Table I) and residual chlorine values obtained by the DPD method were generally smaller than those obtained by the AT and EL methods. Results obtained by two laboratories using the AT method were within ± 6.1% of the mean values. Overall precision for TARC measurements (RSD $\leq$ 10%) was better than that for FARC measurements (RSD $\leq$ 20%), when comparing the AT, DPD, and EL methods.

The residual chlorine measurement methods were further evaluated for application in an extensive monitoring study of water parameters at various stages in three treatment plants. Samples of filter effluent, plant effluent, and tap water were analyzed by the AT, EL, and DPD methods after identical storage periods. The precision of measurements by each method and for all three methods were similar to the results obtained for sodium hypochlorite solutions. DPD method values were again generally smaller than those obtained for the same samples by the AT and EL methods. The precision of TARC values obtained here for sodium hypochlorite solutions and treatment plant water samples compared well with results obtained elsewhere (BENDER 1978) by the same methods for calcium hypochlorite solutions and drinking water.

Typical curves showing the decay of residual chlorine levels in plant effluent water with increasing storage time are plotted

## TABLE I

Comparison of Three Methods for the Determination of Total (TARC) and Free (FARC) Residual Chlorine Levels (ppm) in Aqueous NaOCl.

| Method[b] & Laboratory | Sample, Mean[a] TARC & FARC level (ppm), and RSD (%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 0.8[c] ppm aq. NaOCl | | | | 1.8[c] ppm aq. NaOCl | | | |
| | TARC | | FARC | | TARC | | FARC | |
| | ppm | % | ppm | % | ppm | % | ppm | % |
| AT-A | 0.82 | 1.2 | 0.77 | 0.7 | 1.84 | 1.6 | 1.73 | 0.7 |
| AT-B | 0.75 | 2.8 | 0.75 | 2.3 | 1.63 | 0.7 | 1.60 | 3.1 |
| DPD-C | 0.69 | 6.6 | 0.58 | 16 | 1.57 | 1.7 | 1.39 | 0.8 |
| EL-C | 0.83 | 5.5 | | | 1.80 | 4.2 | | |
| AT-A,DPD-C,EL-C | 0.78 | 10 | 0.68 | 20 | 1.74 | 8.4 | 1.56 | 15 |

[a] Mean values for sets of three samples; blank values of $< 0.03$ ppm substracted. [b] AT, amperometric titration; DPD, DPD ferrous titrimetric; and EL, residual chlorine electrode methods. [c] Approximate TARC level in bulk solution.

in Figure 1. Regression curves (parabola) determined by the method of least squares from results obtained by any two methods were not significantly different ($p < 0.05$) for a particular water sample. Thus, for the water types investigated, residual chlorine values obtained by the three methods will not be significantly different, if analyses are done after the same storage period.

The decay of residual chlorine levels in stored samples was most rapid for recently chlorinated water, e.g. plant effluent, and water samples containing high initial FARC levels. Generally, the difference between TARC and FARC, the combined available residual chlorine, remained constant during most of the storage period. Filter effluent water, with low FARC levels after storage in the clearwell, showed only slight (< 10%) decrease in TARC over 7 hours of sample storage. Tap water, which can be considered as stored plant effluent water, showed significant decrease in TARC over several hours only if initial FARC levels were significant. Thus, as expected, TARC and FARC values obtained for stored water samples are representative of the original sample only if initial FARC levels are very low.

The above results (e.g. Figure 1) indicate that residual chlorine values obtained after sample storage are often not identical to values obtained at the time of sampling. It is recommended (A.P.H.A. 1975) that measurements should be made within 5 min of sampling. Unfortunately, immediate, on-site analyses are often not possible during an extensive monitoring study

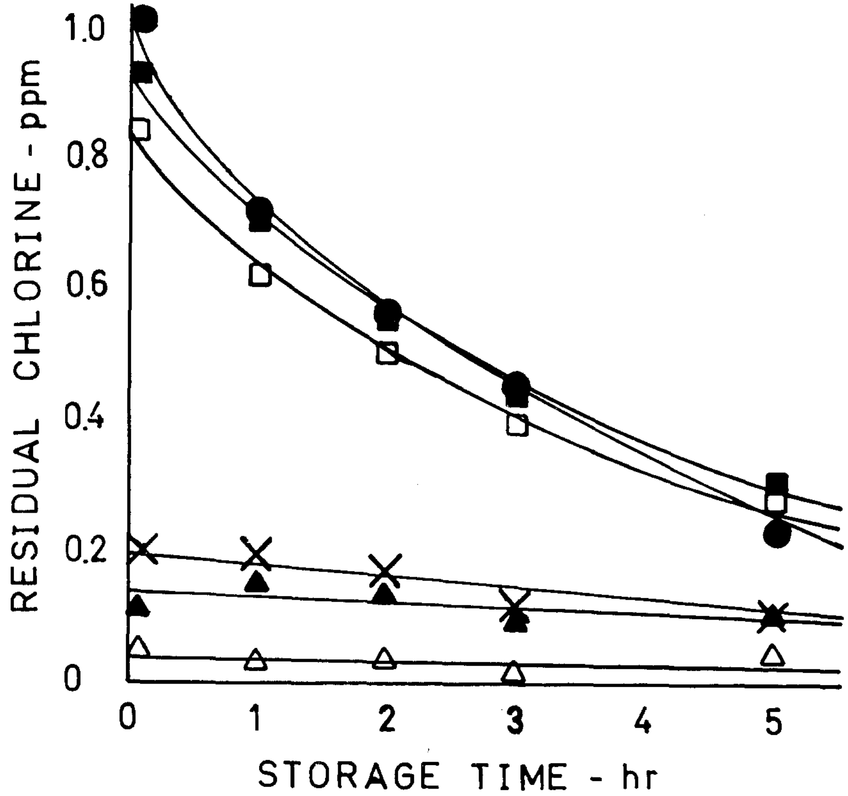

Figure 1. Typical residual chlorine levels in water samples during storage.

Filter effluent: × - TARC by EL-C method; ▲ - TARC, and △ - FARC, by AT-A method.

Plant effluent: ● - TARC by EL-C method; ■ - TARC, and □ - FARC, by AT-A method.

requiring many water samples from different locations. Therefore, the limitations for correlation of residual chlorine values from stored water samples with other water parameters (e.g. trihalomethane levels) was investigated under practical conditions.

Table II summarizes statistical results of typical residual chlorine measurements obtained for treatment system 1 over a 10 month period. The two analytical methods, AT-A and EL-C, which have been shown to give comparable measurements, were also used in a similar study of water in two other treatment systems. The following discussion of results in Table II is also representative of results obtained for the other two treatment systems.

Results of analysis of variance and the correlation coefficients showed that TARC values obtained at different sample storage times by the two methods at different laboratories were not significantly different ($p < 0.05$) and showed good correlation

## TABLE II

Comparison of Residual Chlorine Values Obtained for Stored Water Samples During a Monitoring Study (Treatment System 1).

| Water Type | Method[a] & Lab | Storage[b] Time hr | TARC[c] ppm | FARC[d] ppm | Significance[e] | Correlation Coefficient |
|---|---|---|---|---|---|---|
| Filter Effluent | AT-A | 1 | 0.19 | 0.06 | NS | + 0.962 |
| | EL-C | 3 | 0.21 | | | |
| Plant[f] Effluent | AT-A | 1 | 0.62 | 0.32 | S 0.01 | + 0.679 |
| | EL-C | 3 | 0.44 | | | |
| Tap Water | AT-A | 2 | 0.37 | 0.17 | NS | + 0.888 |
| | EL-C | 3 | 0.37 | | | |

[a] AT, amperometric titration - laboratory A; EL, residual chlorine electrode - laboratory C. [b] Mean values over 11 monitoring days, ranging ± 15 min. [c] Mean values (AT-A method) over 11 monitoring days, ranging: filter effluent, 0.03 - 0.68 ppm; plant effluent, 0.31 - 0.87 ppm; and tap water, 0.12 - 0.59 ppm. [d] Mean values over 11 monitoring days, ranging: filter effluent, 0.00 - 0.30 ppm; plant effluent, 0.14 - 0.57 ppm; and tap water, 0.01 - 0.49 ppm. [e] Results of analysis of variance, significance at $p < 0.05$. NS - not significant, S 0.01 - significant at $p < 0.01$. [f] TARC = 0.90 ± 0.02 ppm (AT-A method) maintained and monitored on-line at treatment plant.

for water samples with low or stabilized FARC values, e.g. filter effluent water. Nevertheless, correlation of other water parameter values with these residual chlorine measurements does not necessarily accurately reflect correlation with residual chlorine values obtained at the time of sampling. Knowledge of the appropriate TARC decay curve is required to determine the relationship between levels present at time of sampling and those present after storage.

The potential danger in using values obtained after storage as representative of values present at the time of sampling is demonstrated by the results for plant effluent water. Here, TARC values were essentially constant (0.90 ± 0.02 ppm, Table II) at the time of sampling, but ranged 0.31 to 0.87 ppm (AT-A method) after 60 ± 15 min of storage.

A significant difference ($p < 0.05$) in values and a relatively low correlation coefficient (+ 0.679) were obtained from stored plant effluent water results. Tap water, which was essentially the above plant effluent stored for longer periods, showed no significant difference ($p < 0.05$) in values and a relatively high correlation coefficient (+ 0.888) for results from samples stored for 2 hr and 3 hr.

## CONCLUSIONS

Sodium hypochlorite solutions, filter effluent, plant effluent, and tap water were analyzed by the amperometric titration (AT), residual chlorine electrode, (EL), and DPD ferrous titrimetric (DPD) methods and the results were compared for the range 0.2 to 2.0 ppm residual chlorine. Overall precision for measurements by all three methods and in three laboratories was $\leq$ 10% RSD for TARC and $\leq$ 20% for FARC. Amperometric titration was judged the method of choice because of precision of measurements, simplicity of operation, and capability for both TARC and FARC determinations.

A rapid initial decay of TARC in stored water samples containing high initial levels of FARC was observed. Residual chlorine values obtained from such samples after storage could not be meaningfully correlated with other water parameters obtained during the monitoring study. Correlation was only meaningful for water samples which did not show a significant change in residual chlorine levels after storage.

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