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TECHNICAL NOTE

GRAVIMETRIC SAMPLING PROCEDURE FOR AQUEOUS OZONE CONCENTRATIONS

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Abstract—Sampling procedures for the standard method for measuring dissolved ozone concentrations in water were modified by replacing narrow-necked volumetric flasks with wide-necked Erlenmeyer flasks, followed by gravimetric determination of sample volume. The intent of these modifications was to improve sampling ease, speed, and reproducibility when collecting large number of samples with highly variable and rapidly decaying dissolved ozone concentrations. Subsequent comparisons between samples collected by the standard method and the modified gravimetric method showed greater apparent ozone concentrations in samples collected by the modified method. This difference appears to result from negative sampling biases when using volumetric glassware under typical full-scale sampling conditions. © 2000 Elsevier Science Ltd. All rights reserved

Key words—ozone residual, indigo trisulfonate, gravimetric sampling

INTRODUCTION

Previous studies have extensively demonstrated the utility of indigo trisulfonate as an analytical reagent for the determination of dissolved ozone concentrations in water (Bader and Hoigné, 1981, 1982). The relatively simple colorimetric technique, based on the rapid bleaching of an acidic indigo trisulfonate solution in the presence of ozone, has been shown to be as precise and accurate as other analytical methods, even in the presence of other oxidants under conditions likely to be encountered during water treatment (Grunwell *et al.*, 1983; Gordon *et al.*, 1988).

As described in *Standard Methods* (Method 4500-O_3), the use of 100 ml volumetric flasks is advocated for the collection of fixed volume ozone concentration samples (APHA, 1995). This specification is intended to simplify both sample collection and subsequent concentration calculations. However, the use of the fixed volume sampling procedure can be problematic when sampling rapidly varying ozone concentrations. These conditions are often found when sampling large-scale ozone contactors, particularly at locations near gas diffusers, flow partitions, and other locations with unsteady hydrodynamic flow patterns (AWWARF, 1995). Under these sampling conditions, rapid changes in ozone concentrations can easily result in either underbleaching or overbleaching of the indigo reagent solution.

Additional difficulties with the fixed volume sampling procedure are encountered when sampling waters which exhibit rapid ozone decay. These conditions often result during the oxidation of waters containing reactive compounds such as dissolved organic matter or hydrogen peroxide. Under these ozonation conditions, the use of standard method sampling procedure when sampling full-scale contactors results in extensive ozone decay prior to reaction with the indigo reagent. Furthermore, the collection of replicate samples may not be feasible, given the rate of ozone decay and the time period required to collect a single standard method sample.

In concept, variable volume sampling procedures can mitigate some of these difficulties (Bader and Hoigné, 1981; Chiou *et al.*, 1995). With these methods, only the volume of ozonated water required to partially bleach the indigo reagent is rapidly added to the sampling flask (Bader and Hoigné, 1981). In one possible method, ozonated water is added directly into the indigo reagent in a wide-necked sampling flask, followed by gravimetric

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determination of sample volume. The advantages to this sampling procedure are that it simplifies and speeds sample collection, minimizes underbleaching and overbleaching of the indigo solution, and eliminates the use of dilution water. Furthermore, these sampling modifications can improve accuracy and precision as they eliminate the use of pipettes and overflowing sample collection flasks. Under typical pre-ozonation sampling conditions, the use of volumetric glassware may result in substantial ozone decay, offgassing, and sample homogenization. These modifications also "ruggedize" sample collection by eliminating the use of fragile volumetric flasks and pipettes. These modifications alone are particularly advantageous when collecting samples outside of the laboratory.

To evaluate these possible sampling modifications, side-by-side testing was conducted with the standard method. To ensure a fair trial, relatively stable ozone concentrations (conditions under which the standard method was developed and optimized), were used throughout this testing.

MATERIALS AND METHODS

Type II indigo trisulfonate reagent solution (Aldrich) was prepared as described in *Standard Methods* (APHA, 1995). The volume prepared (3.5 l) was sufficient to last throughout all testing. Ten milliliters of indigo reagent was added to each sample flask using an adjustable volume bottle-top dispenser (Brinkmann Dispensette). Indigo reagent was added to the two types of sampling flasks in an alternating fashion to minimize any possible filling bias. The accuracy of the dispenser was checked gravimetrically on a frequent basis.

Samples collected by the procedures described in *Standard Methods* were designated as volumetric samples. For high ozone concentration samples, ozonated water was added directly to the volumetric flask, followed by the addition of dilution water using a graduated pipette. Samples collected by the modified method were designated as the gravimetric samples. For these samples, sufficient ozonated water was added to indigo reagent solution in a 125 ml Pyrex® Erlenmeyer flask to bleach/dilute the indigo solution to a light blue color ($A_{600} \geq 0.050$ cm^{-1}), followed by gravimetric determination of sample volume using a portable electronic scale (Ohaus Model C305). The accuracy of this instrument ($\pm$0.1 g) was checked with a 200 g calibration weight, which was close to the final weight of sampled flasks. Additionally, the accuracy of the scale was cross-checked by the filling of 100 ml volumetric flasks (Pyrex® Class A).

Ozonated water samples were collected from a pilot-scale water treatment plant employing pre-ozonation at a dose of 2.0 mg/l. High ozone concentration samples (>0.5 mg/l) were collected directly from the effluent of the pilot-scale ozone contactor. Moderate ozone concentration samples (<0.5 mg/l) were collected downstream from the ozone contactor, at the entrance to the conventional treatment plant. Samples for the two methods were collected in an alternating manner to minimize possible sampling bias. The sample flow rate during all testing was maintained at $\sim$750 ml/min, which is near the upper flow rate for accurate filling of the volumetric flasks. In contrast, flow rates as high as 2500 ml/min can be maintained when sampling with wide-necked Erlenmeyer flasks.

Sample absorbance was measured at 600 nm using a bench-top dual-cell spectrophotometer (Perkin–Elmer Lambda 3B). All samples were analyzed within an hour of sampling. Samples collected by the two methods were analyzed in alternating fashion to minimize the possible impact of analytical drift on the apparent measurements. Rectangular quartz cuvets with an optical path of 10 mm were used in place of the recommended 50 or 100 mm cylindrical cells. This was due to the ability to scrupulously clean the rectangular cuvets after extensive use.

Ozone concentrations for the volumetric samples were calculated as described in *Standard Methods* (APHA, 1995). Gravimetric sample ozone concentrations were calculated using the equation

$$O_3(mg/l) = \frac{(A_{600} \times V_T)_{blank} - (A_{600} \times V_T)_{sample}}{V_S \times 0.42 \times b}$$

where A_{600} is the sample absorbance at 600 nm; V_T is the total volume (ml); V_S is the sample volume (ml); and b is the optical pathlength (cm).

As shown, the modified equation is a more general form of the equation found in *Standard Methods*. Statistical parameters were calculated using standard spreadsheet functions (Borland Quattro Pro 5.0).

RESULTS

Figure 1 shows the apparent ozone concentrations resulting from the two sampling methods at moderate ozone concentrations. Ninety-milliliter volumes were collected for the volumetric samples. Sample volumes ranging from 45 to 67 ml were collected for gravimetric samples (see Table 1). As shown, samples collected by both methods show similar fluctuations about their respective mean concentration, suggesting similar sensitivities to variations in ozone concentrations. However, apparent ozone concentrations measured by the gravimetric method are consistently greater than those concentrations derived from samples collected with volumetric glassware. A second set of ozone concentration samples collected by a second analyst gives similar results (see Table 1). For both data sets, mean gravimetric ozone concentrations were approximately 0.06 mg/l or 15% greater than the mean standard method ozone concentrations. Results of *t*-test analysis suggest that the difference in mean apparent ozone concentrations resulting from the two sampling methods is statistically significant at greater than the 99% confidence level.

Figure 2 shows the apparent ozone concentrations resulting from the two sampling methods at higher ozone concentrations. Under these ozonation conditions, much smaller sample volumes ranging from 29 to 35 ml were required for both sampling methods. Again, similar variations and trends in ozone concentrations are observed for both sampling methods. In contrast to previous results, little difference in apparent ozone concentrations was found between the two sampling methods at high ozone concentrations (see Table 1). Samples collected by the gravimetric method have only a slightly greater mean and lower standard deviation.

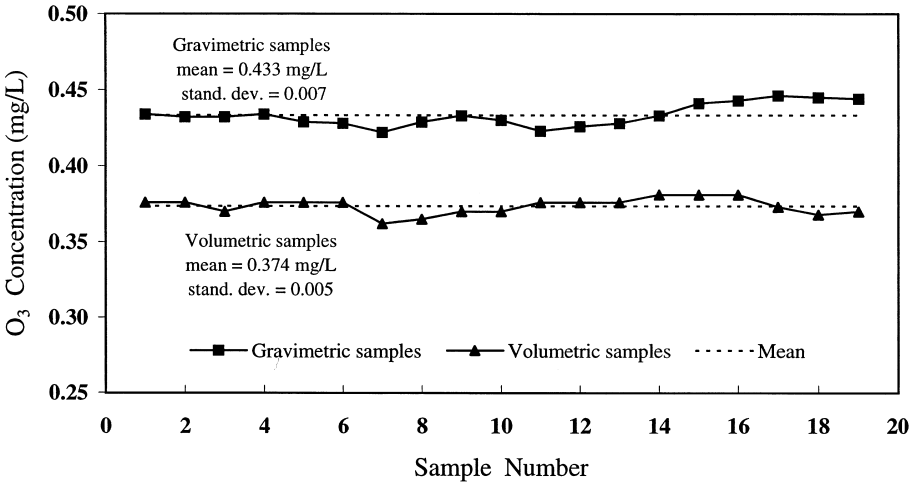

Fig. 1. Comparison of dissolved ozone concentration trends resulting from gravimetric and volumetric sampling methods at moderate ozone concentrations.

Statistical comparison shows this difference to be significant at only the 90% confidence interval.

The relatively large percentage difference in apparent ozone concentration observed at moderate concentrations in this study for samples collected by the two sampling methods appears to result from negative sampling biases when collecting large sample volumes (90 ml) with narrow-necked sampling flasks. Under typical sampling conditions, ozone loss may result from offgassing of volatile gases during turbulent thin-layer flow of the sample along the inside of the neck of the volumetric flask. Additionally, ozone loss may be due to decomposition prior to bulk mixing with indigo reagent. This may be particularly true during the slow neck-filling portion of the sampling process.

In contrast, the relatively small difference in apparent ozone concentration found at high concentrations appears to result from the collection of relatively small sample volumes for the volumetric method. The collection of smaller sample volumes reduces the magnitude of ozone loss due to offgassing. Furthermore, collection of these small sample volumes eliminates the possible loss of ozone during the neck-filling portion of the sampling process. These combined effects result in a minimal difference in mean ozone values between the two sampling methods.

It should be noted that both possible sources of ozone loss (offgassing and decomposition) could be controlled by routing ozonated water directly into the indigo reagent (using a pipette or flexible non-reactive tubing). However, sampling under these conditions requires sample flow rates as low as ~250 ml/min to accurately fill volumetric flasks. As such, this sampling method would be appropriate only for waters with low and moderate ozone concentrations exhibiting very slow ozone decomposition and little spatio-temporal variation.

CONCLUSIONS

The gravimetric sampling procedures discussed in this paper simplify and ruggedize the sampling of dissolved ozone concentrations by eliminating the use of fragile and cumbersome glassware. These sampling modifications result in improved analytical accuracy and precision over a wide range of ozonation conditions, and restore much of the flexibility as initially described for the indigo method (Bader

Table 1. Comparison of dissolved ozone concentrations resulting from gravimetric and volumetric sampling procedures

Trial	1		2		3	
Ozone concentration range	Moderate		Moderate		High	
Sampling method	Gravimetric	Volumetric	Gravimetric	Volumetric	Gravimetric	Volumetric
Number of samples	19	19	20	20	10	10
Sample volumes (ml)	53–67	90	47–65	90	29–34	29–35
Mean O_3 concentration (mg/l)	0.433	0.374	0.453	0.393	1.12	1.08
Standard deviation	0.007	0.005	0.005	0.004	0.04	0.06
Coefficient of variation (%)	1.6	1.3	1.1	1.0	3.6	5.6
Difference between means (%)	15.8	–	15.3	–	3.7	–
Probability ($T < t$)	$\ll$0.1	–	$\ll$0.1	–	9.1	–

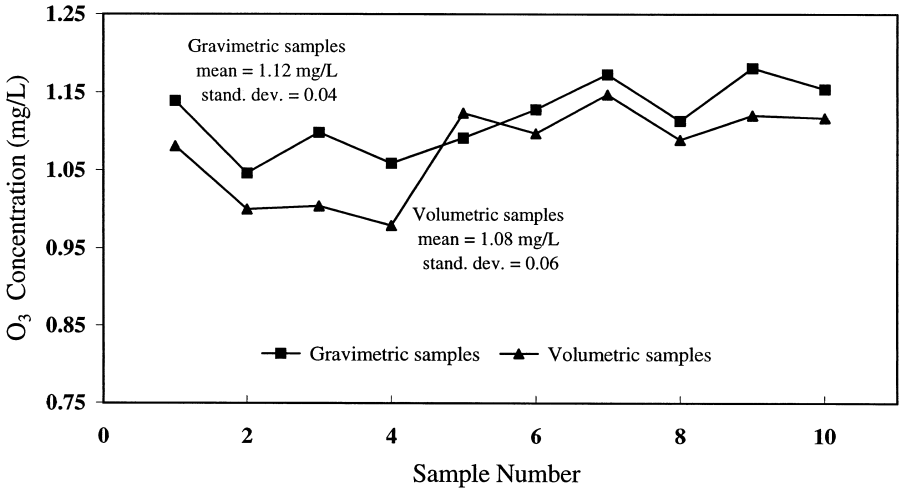

Fig. 2. Comparison of dissolved ozone concentration trends resulting from gravimetric and volumetric sampling methods at high ozone concentrations.

and Hoigné, 1981). Based on the differences observed in apparent ozone concentrations (even under stable ozone conditions), caution should be exercised when using volumetric glassware to sample dissolved ozone concentrations.

For utilities which typically operate at moderate ozone concentration, the gravimetric sampling method will eliminate underestimation in ozone concentration which may result from use of the current standard method. Use of the gravimetric method may result in the reduced application of ozone (15% or more at moderate doses) to meet existing disinfection and oxidation targets. In turn, this may reduce operating costs and oxidation byproduct formation. Furthermore, the simplified sampling procedure results are likely to result in improved agreement in sampling results between laboratory analysts and operators. For researchers, use of the gravimetric sampling protocol can reduce the sample volume and concomitant sample loss which occurs during extensive testing. As such, this method may provide more frequent and more accurate samples, resulting in greater data resolution. This is particularly true when sampling over a wide range of ozone concentrations and conditions.

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