

Laboratory Validation of Ozone Sampling with Spill-Proof Impingers



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Laboratory Validation of Ozone Sampling with Spill-Proof Impingers

Research performed by the Southern Research Institutes, Birmingham, Alabama, under contract with the American Welding Society and supported by industry contributions.

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Abstract

This report describes the adaptation of an existing air sampling and analytical method for ozone to the personal monitoring of employee exposures to the substance inside a welding helmet. The Saltzman iodometric method was modified to accommodate helmet sampling. The personal air sampler that was developed consists of a Teflon filter in a polystyrene holder joined with flexible tubing to a spill-proof impinger containing an alkaline potassium iodide solution. The sampler is compatible with a personal sampling pump capable of an air flow rate of 2.0 L/min.

The overall method was evaluated in the laboratory with ≈ 110 -L test atmosphere samples at an ozone concentration of about 0.1 ppm (0.2 mg/m³ at 25° C) and with ≈ 40 -L test atmosphere samples over the concentration range of 0.3 to 5.1 ppm (0.6 to 10 mg/m³ at 25° C). The average bias relative to an independent sampling method was about -10% for determinations near 0.1 ppm and about +7% for determinations in the range of 0.3 to 5.1 ppm. The relative standard deviation at 0.1 ppm was 6.6% and the pooled relative standard deviation for concentrations in the range of 0.3 to 5.1 ppm was 7.7%.

Field tests of the method were not as successful. The ozone concentrations determined with the developed method were much lower than those simultaneously determined with a chemiluminescent monitor and those determined by another iodometric impinger method, the boric acid/potassium iodide method. Loss of ozone as a result of reaction with welding fume present in the air samples or as a result of the catalysis of other reactions of ozone by the fume may have contributed to the observed discrepancies. A tentative personal sampling and analytical method was recommended based on the boric acid/potassium iodide procedure.

Laboratory Validation of Ozone Sampling with Spill-Proof Impingers

I. Background and Research Approach

A. Background

All arc welding operations produce ultraviolet radiation; in turn, the ultraviolet rays with wavelengths <210 nm photolyze oxygen to ozone.¹ The amount of ozone formed depends on the intensity of the ultraviolet radiation. Without adequate ventilation, hazardous concentration levels of ozone (i.e., levels greater than the Federal permissible exposure limit of 0.1 ppm) may accumulate not only near the arc but also some distance away from the arc.

To avoid exposures of welders to hazardous levels of ozone, it is necessary to monitor the concentration of the substance in the air that they breathe. Air samples taken with a sampler attached to the welder's shirt lapel (a typical location for personal sampling) are not necessarily representative of the exposure of that individual to ozone because he breathes not the air outside in the workplace but rather the air inside his welding helmet. One definitive study of the formation of ozone during various arc welding processes indicated that the helmet provided the welder with significant protection from exposure to ozone.² For example, concentrations as high as 8.4 ppm of ozone in air were found outside the helmet when aluminum was welded by the argon-shielding technique; however, inside the helmet, the ozone concentration was found to be 0.47 ppm.

Because there was no validated air sampling and analytical method available for the determination of ozone in air inside a welding helmet, we modified an existing method and designed a personal sampler applicable to sampling inside a helmet. The American Welding Society (AWS) supported our laboratory development and evaluation of the method and our field tests, which are described in detail in the subsequent sections of this report.

B. Research Approach

1. Purpose and General Considerations

One primary emphasis of our work was to develop and evaluate a suitable personal sampler. At the request of the AWS, the sampler was to consist of the following components (in the order of their occurrence in the sampling train):

- a particulate filter in the helmet to remove welding fume from the air sampling stream,
- flexible tubing for the transport of ozone from the helmet to an absorbing solution, and
- a spill-proof impinger containing the absorbing solution.

A second major goal of the project was to choose a suitable existing impinger sampling and analytical method that could be adapted for the personal sampler being developed and to evaluate the performance of the adapted method. Because the sorption and preservation of ozone intact in an impinger solution was unlikely, we assumed that the method of choice would involve the reaction of ozone to form a reasonably stable product. As part of the evaluation of the method, we were to determine the storability of the reaction product.

Our general experimental approach involved several steps: First, we performed a literature search for information relating to air sampling and analytical methodology for ozone. Second, we devised an experimental protocol for the adaptation of an existing method to a personal sampling and analytical method for determining ozone inside a welding helmet. The protocol was reviewed, revised, and approved by the AWS; subsequently, a modified method was developed and evaluated according to the revised protocol as described in Section I.B.3 of this report.

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2. Literature Search

The literature search was directed toward the following two topics:

- a survey of ozone sampling methods including methods using flexible tubing and
- a survey of the past studies involving problems associated with the storage and handling of sampling media exposed to ozone.

The resulting information relating to the affinity of ozone for various types of flexible tubing indicated that ozone exhibited little affinity for Teflon tubing; however, contradictory evidence was reported for other types of tubing. In the validation of a method for ozone for the National Institute for Occupational Safety and Health (NIOSH), a Teflon sampling manifold was employed without difficulty for the transfer of test atmospheres containing 0.05 to 0.2 ppm of ozone.³ Altshuller and Wartburg found that Teflon passed ozone without loss, but that polyethylene, Nalgon, and some types of PVC tubing were unsatisfactory for passing ozone.⁴ Cohen et al. found that 60-cm (24-in.) lengths of 6-mm-i.d. poly(vinyl chloride) (PVC), 5-mm-i.d. polyethylene, and 5-mm-i.d. nylon tubing sorbed only a small fraction ($\leq 7\%$) of the ozone sampled through the tubes at 2 L/min for 20 min from an atmosphere containing 0.2 ppm of ozone.⁵ Another source, however, stated flatly that ozone is destroyed by contact with PVC.⁶ Consequently, we decided that our work should include the investigation of Teflon tubing, at least initially. Other materials were to be tested only if Teflon was found to be unsuitable during the evaluation.

The literature search also revealed that the most appropriate choice of an existing impinger sampling and analytical method for adaptation was the alkaline potassium iodide (AKI) method originally developed by Saltzman.⁷ A major advantage of this method was the reported stability of the reaction product of ozone with the absorbing reagent; however, little evidence was given to support this claim. NIOSH validated the method for 45-L air samples in an ozone concentration range of 0.05 to 0.2 ppm (0.1 to 0.4 mg/m³ at 25° C).⁸

Several disadvantages of the Saltzman procedure were also reported⁷: Other oxidants, such as nitrogen dioxide, were reported to cause positive interferences. The interference of nitrogen dioxide, however, was limited to 10% of that expected on a mole-to-mole equivalency by the use of sulfamic acid to destroy nitrite ion in the impinger solution. In another reported method (i.e., the neutral buffered potassium iodide method (NBKI), the degree of interference by nitrogen dioxide was quantified.⁵ Sample air was drawn through two parallel impingers containing the iodometric reagent; however, upstream from one of the impingers, the air was passed through a tube containing cotton wool. The wool reacted with ozone, but

nitrogen dioxide passed through the wool into the attached impinger. In the subsequent analyses of the impinger solutions, the response obtained with the solution exposed to nitrogen dioxide but not to ozone was subtracted from that for the other sample solution to yield the response attributed to ozone.

It was also reported that negative interferences in the Saltzman procedure are produced by reducing agents such as nitric oxide, sulfur dioxide, and hydrogen sulfide.⁷ The sulfur dioxide interference can be removed by incorporating into the sampling train, upstream from the impinger, a glass-fiber filter impregnated with chromium trioxide; however, the filter will also convert nitric oxide to nitrogen dioxide and thereby produce the positive interference cited above.

In spite of its shortcomings, the Saltzman AKI procedure appeared to be more suited to the desired application than did other techniques. Other iodometric methods—the NBKI method and the boric acid-potassium iodide (BAKI) method—were considered to be less appropriate because iodine is liberated as ozone is collected.^{6,9,10} On-site spectrophotometric measurements would therefore be required; in the welding industry, however, field spectrophotometric measurements may often be impractical. In another technique, ozone was reacted with 1, 2-di-(4-pyridyl) ethylene in chloroform to yield pyridine-4-aldehyde, which was determined fluorometrically after reaction with 2-diphenylacetyl-1, 3-indandione-1-hydrazone.¹¹ The method was specific for ozone; however, the efficient collection of ozone required that the absorbing solution be maintained at -18° C. Also, the reaction between ozone and the reagent was found to be sensitive to water. These two disadvantages appeared to make the method impractical for field sampling. Yet another procedure involved the reaction of ozone with eugenol to form formaldehyde and the subsequent determination of formaldehyde by a modification of the West-Gaeke procedure for sulfur dioxide. This method appeared to be unsatisfactory because it was reported that as much as a 20% decrease in the concentration of formaldehyde in field samples was observed after storage for 7 d.

3. Protocol

On the basis of the information found during the literature search and other practical considerations expressed by the AWS, we formulated a workplan. The protocol consisted of explicit experimental plans to develop a suitable personal sampler and to evaluate the Saltzman AKI method as adapted for use with the developed sampler. The major tasks involved in the workplan were as follows:

- construction and evaluation of an ozone test atmosphere generator,
- development of the prototype sampler,

Research Approach/3

- validation of the modified ozone sampling method,
- determination of the storability of sample solutions, and

- field evaluation of the modified ozone sampling method.

The subsequent sections of this report describe the test procedures and present the resulting data.

II. Construction and Evaluation of an Ozone Test Atmosphere Generator

A test atmosphere generator was required for the evaluation of sampling devices. We designed the generation system to provide test concentrations of ozone over wide ranges and at relative humidities between 10 and 80 to 90%.

A. Construction of the Generator

The generation system is depicted in Fig. 1. Dry, filtered air was flushed over a mercury vapor lamp and this "ozonized" air combined with additional air in the mixing chamber to obtain the test atmosphere.

To eliminate potential problems with contamination, the compressed air supply was cleaned prior to introduction into the system. The air was first passed through an oil trap and then dried with a Puregas Heatless Dryer obtained from Puregas Equipment Company, Capiague, New York. (The dryer contained beds of molecular sieves for removing water vapor). The air was then passed sequentially through manganese dioxide, firebrick impregnated with chromium trioxide, and finally a bed of charcoal.

The dry dilution air was rehumidified by metering a portion of the dilution airstream through a heated Greenburg-Smith impinger containing distilled, deionized water and by then mixing the humidified air-

stream with the appropriate proportion of dry air to obtain the desired relative humidity. The humidified air was transferred to the mixing and sampling chambers through heated Teflon tubing to avoid condensation of the water vapor.

The ozone was produced by the photolysis of diatomic oxygen in air with an Hanovia 550-W high-pressure mercury vapor lamp. The lamp was housed in a watercooled quartz tube, which was itself housed within a Pyrex glass tube. Nitrogen was flushed around the water-jacketed quartz tube to prevent the production of ozone outside the quartz tube.

The ozone and air mixture was passed into a cylindrical glass sampling chamber, a Pyrex glass pipe of 6-in. length by 4-in. o.d. with Teflon discs for end caps. The ozone test atmosphere entered the sampling chamber through an opening in the top cap of the vertically mounted chamber. Seven sampling ports and a vent were located in the bottom cap.

The sampling system was arranged so that test air could be sampled into impingers while simultaneously being sampled into a chemiluminescent ozone monitor, the Meloy Model 350-2R Ozone Analyzer. Sampling rates of 1 to 2 L/min for the sampling device were maintained with critical flow orifices attached to a vacuum pump.

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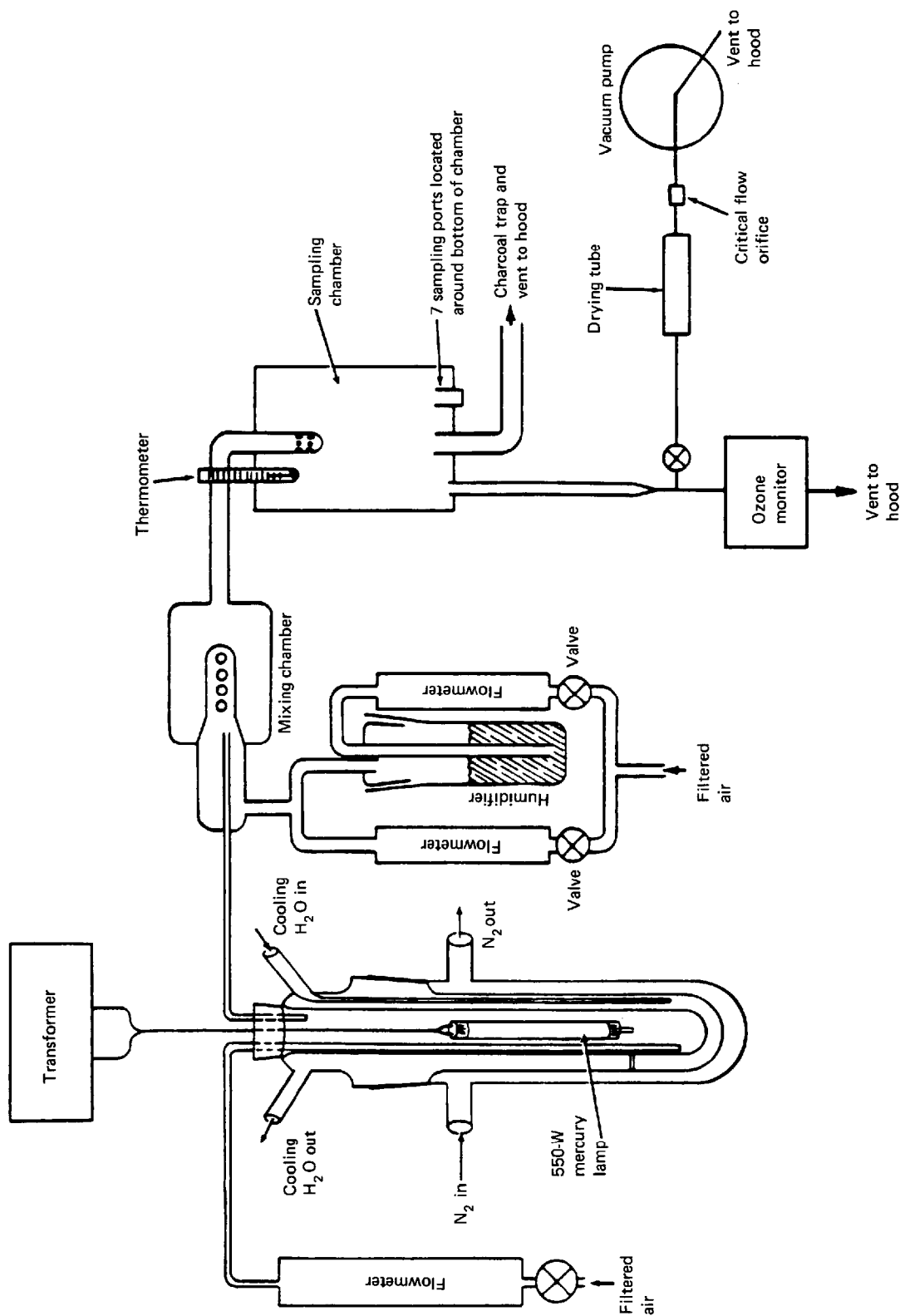


Fig. 1 — Ozone test atmosphere generator

B. Evaluation of the System

To evaluate the performance of the test atmosphere generator, the volume flow rate of air passing through the ozonizer (i.e., the UV lamp and its housing) and the volume flow rate of the dilution air were varied while generator effluent was sampled with the Meloy monitor. The flow rate was varied from 6 to 18 L/min. The total flow rate ranged from about 9 to 18 L/min. In one experiment, the relative humidity of the test atmosphere was maintained at 70%; in all other tests, the relative humidity was $\leq 10\%$. The sampling line connecting the monitor with the chamber was a 4-ft length of Teflon tubing with a 0.125-in. o.d. and a 0.06-in. i.d. This tubing was provided by the manufacturer and was employed as a sampling line during the calibration of the instrument by the manufacturer. The monitor response was registered on a potentiometric strip-chart recorder.

The ozone concentrations recorded by the monitor ranged from 0.1 to 5.9 ppm. For each set of sampling conditions, the generator output generally did not fluctuate any more than about $\pm 5\%$ from an average response level. In one typical 4-h period, the ozone

concentration averaged 0.103 ppm, with a relative standard deviation (RSD) of 2.4%.

The ozone concentration was found to be related to the air volume flow rate in a reasonably predictable manner. In Fig. 2, the observed ozone concentrations are plotted as a function of the quotient of the flow rate through the ozonizer and the total volume flow rate. A linear least-squares fit is also presented; the line was used to estimate the ratio of flow rates required to generate a particular concentration of ozone.

An increase in the relative humidity of the test atmosphere from 10 to 70% at an ozone concentration of about 0.25 ppm did lower the response of the monitor somewhat. Over a period of about 1 h, the meter reading decreased from about 0.25 to 0.22 ppm, a change of $\approx 10\%$.

From the results of the evaluation tests described above, the generator was judged to be suitable for producing stable test atmospheres of ozone in air for the validation of a sampling and analytical method for ozone.



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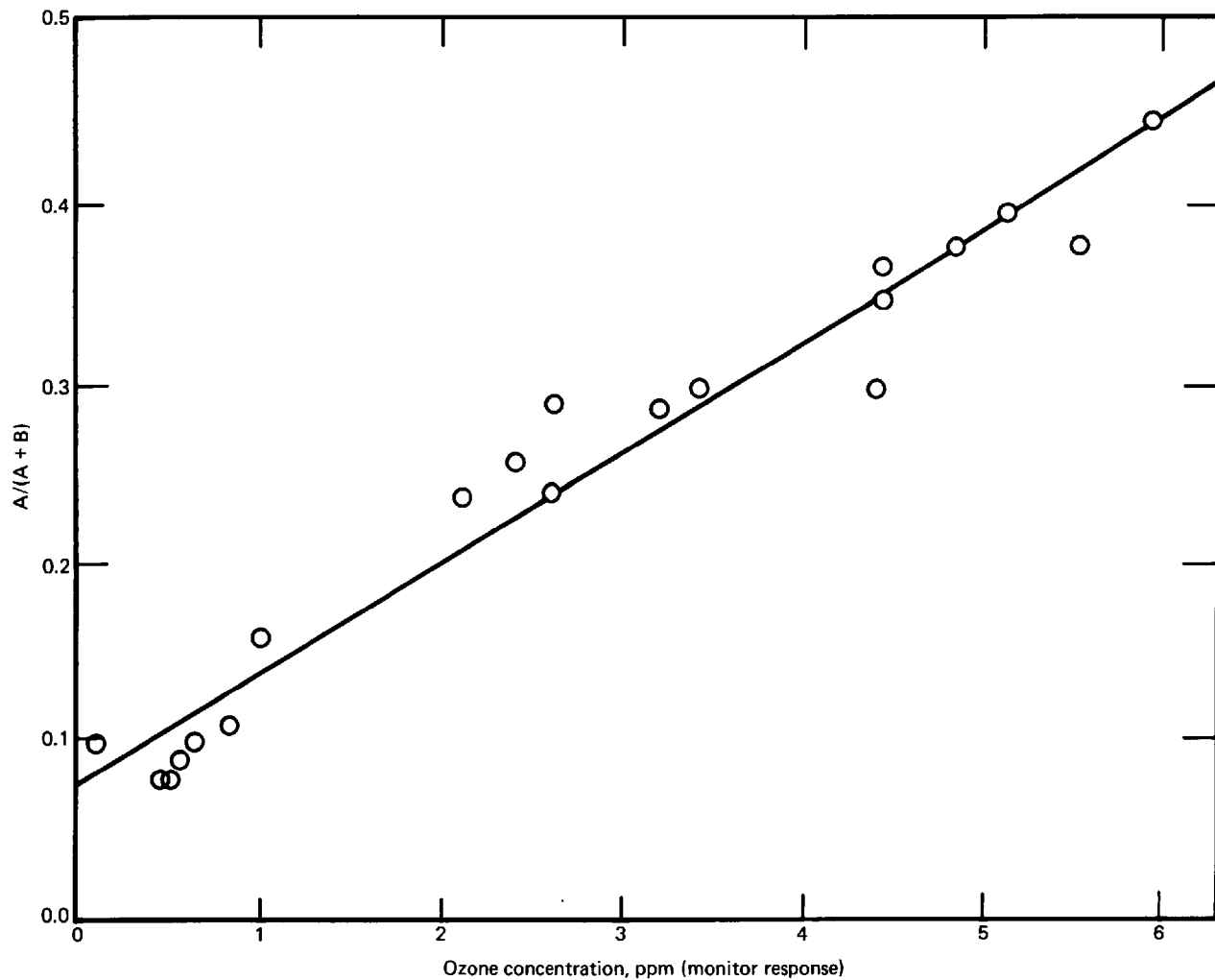


Fig. 2 — Ozone concentration in the generator effluent as a function of the volume flow rate of ozonized air (A) and the volume flow rate of dilution air (B)