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To cite this article: E.B. DOWNEY , R.M. BUCHAN , K.D. BLEHM & B.J. GUNTER (1983) A Comparison of Two Ozone Sampling Methods, American Industrial Hygiene Association Journal, 44:5, 333-335, DOI: [10.1080/15298668391404923](https://doi.org/10.1080/15298668391404923)

To link to this article: <https://doi.org/10.1080/15298668391404923>



Published online: 04 Jun 2010.



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A Comparison of Two Ozone Sampling Methods

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A study was conducted to compare the alkaline potassium iodide (AKI) impinger method versus a direct-reading chemiluminescent monitor for determining ozone concentrations. Comparisons were made in both a controlled laboratory situation and in the field during MIG welding. Laboratory results indicated that the accuracy of the AKI procedure is affected by sample size. In the field, AKI impinger samples seemed to give very low estimations of the true ozone concentration. The direct-reading chemiluminescent monitor performed excellently in both the laboratory and field, and exhibited its merit as an industrial hygiene field instrument.

Introduction

Occupational exposure to ozone may present a problem during gas-shielded arc welding when ozone is formed by the reaction between ultraviolet light from the welding arc and oxygen in the air.⁽¹⁾ Health complaints associated with ozone exposure include nose and throat irritation, cough, chest pain, and other respiratory effects.⁽²⁾ Chronic exposure to low levels of ozone has been implicated in the occurrence of chromosomal aberrations.⁽³⁾ The American Conference of Governmental Industrial Hygienists has recommended a threshold limit for occupational exposure of 0.1 ppm ozone as an eight-hour time-weighted average.⁽⁴⁾

Detection of small quantities of ozone in the air is a difficult problem. The present impingement method [colorimetric-alkaline potassium iodide (AKI)] that is widely used is subject to serious interferences from oxidizing and reducing gases. Additionally, the National Institute for Occupational Safety and Health (NIOSH) has only validated the method over an ozone concentration range of 0.05 to 0.20 ppm.⁽⁵⁾ Several direct-reading ozone monitors are currently available that utilize the chemiluminescent reaction of ozone and ethylene. These instruments have been demonstrated to be specific to ozone and subject to few interferences.⁽⁶⁾ The objective of this study was to compare the reference impinge-

ment method versus a direct-reading chemiluminescent monitor [Analytical Instrument Development, Incorporated (AID) Model 560 ozone analyzer] for determining ozone concentrations during metal inert gas (MIG) welding.

Materials and Methods

Preliminary comparisons of the sampling methods were conducted in the laboratory using an ozone generator that had been calibrated using the Environmental Protection Agency reference technique of ultraviolet photometry.⁽⁷⁾ This allowed for determinations of the accuracy and precision of the two methods in standard ozone atmospheres. Additionally, in the laboratory the effect of sample size on the accuracy of the AKI procedure was evaluated.

Field sampling was conducted during MIG welding of mild steel. The use of different ventilation rates and welding amperages allowed for comparisons to be made over a wide range of ozone concentrations. Concomitant samples were taken through side-by-side closed-face filter cassettes mounted on the face of the welder's helmet. The cassettes were connected by eight-foot lengths of 0.125-in. I.D. Teflon[®] tubing to an impinger and the AID monitor. The cassettes were

TABLE I
Precision of AID and AKI Methods Versus Reference UV Photometer

Number of Trials	Ozone Concentration (ppm ^A)				
	UV ^B Photometer	AID ^C Mean Concentration	Standard Error	AKI ^D Mean Concentration	Standard Error
9	0.052	0.042	0.009	0.048	0.005
9	0.201	0.199	0.002	0.203	0.022
9	0.802	0.800	0.007	0.765	0.045
9	1.61	1.61	0.028	1.58	0.095

^Appm - parts per million (volume).

^BUsed as reference measurement method.

^CAID Monitor sampling rate = 0.66 L/min.

^DAlkaline potassium iodide (AKI) impinger sampling rate = 1.0 L/min.

TABLE II
Ozone Concentrations Found by Two Sampling Methods in Air Samples Taken During MIG Welding

Sample Run Number	Sampling Time (min)	Ozone Concentration ^A from Impinger (ppm)	Ozone Concentration ^B from AID Monitor (ppm)	Agreement ^C between Methods (%)	Mean Agreement between Methods (%)
1	44.0	0.042	0.072	58.8	
2	44.0	0.048	0.090	53.3	
3	44.0	0.046	0.084	54.8	56.7
4	44.0	0.041	0.075	54.7	(sample runs 1-5)
5	44.0	0.046	0.074	62.2	
6	8.00	0.203	1.54	13.2	
7	8.00	0.131	1.32	9.9	
8	2.00	0.541	4.80	11.3	11.9
9	6.17	0.281	1.82	15.4	(sample runs 6-10)
10	9.50	0.146	1.46	10.0	

^AAlkaline potassium iodide (AKI) impinger sampling rate = 1.0 L/min.

^BAID Monitor sampling rate = 0.66 L/min.

^CAgreement - (Impinger concentration/AID concentration) × 100.

loaded with 0.45- μ m Teflon filters to remove welding fume from the sampled air. Welding fume was gravimetrically determined for each sample taken. Since nitrogen dioxide (NO₂) can create a small positive interference in the AKI procedure, NO₂ levels were monitored using a Miran infrared analyzer.

Sampling was initiated and terminated simultaneously for the two ozone sampling techniques. A record of the ozone concentration measured by the AID monitor was obtained by connecting the instrument to a strip chart recorder. During sampling, the welder struck an arc for two-minute periods interspersed with two-minute rest intervals. For sample runs 1-5, sampling was conducted long enough to draw approximately 45 liters of air (standard AKI sample volume) through the impingers at a sampling rate of 1.0 L/min. The sampling rate for the AID monitor was 0.66 L/min. For sample runs 6-10, impinger samples were run long enough to collect the approximate ideal sample size (μ g of O₃) that had been determined in the laboratory. This time period was estimated by examining the AID strip chart recording of the ozone concentration while sampling was in process. Ozone concentrations measured by the impinger samples were determined the following day in the laboratory. Ozone was quantitated from the AID monitor by integrating the area under the curves of the strip chart recordings. The accuracy and precision of the AID chemiluminescent monitor and the AKI impingement procedure is shown in Table I. Both methods were evaluated versus a reference ultraviolet photometer operating at a wavelength of 254 nanometers (nm).

Results and Discussion

In the laboratory, the AID monitor exhibited excellent accuracy and precision at ozone test concentrations of 0.052, 0.201, 0.802 and 1.61 ppm. AKI impinger samples taken at the same ozone concentrations showed more variability (see Table I). Mean impinger accuracy (percent agreement with

true ozone concentration) for all four ozone concentrations combined was 84.0%, 98.1% and 107% for sample sizes of 5, 15 and 25 μ g of ozone, respectively. Based on laboratory results, a sample sized of 15 to 25 μ g of ozone was determined to yield the best results for the AKI procedure.

Sampling results obtained during MIG welding are presented in Table II. For sampling runs 1-5, the ozone concentration, as determined by the AID monitor, ranged from 0.072 ppm to 0.090 ppm. Ozone concentrations obtained by the AKI procedure were significantly lower, ranging from 0.042 ppm to 0.048 ppm. The percent agreement between the two sampling methods ranged from 53.3% to 62.2%, and the mean agreement was 56.7%.

For sampling runs 6-10, reduced ventilation and increased welding amperage resulted in extremely high ozone levels. The AID monitor measured ozone concentrations ranging from 1.32 ppm to 4.80 ppm. Therefore, the sampling time needed to collect 15 to 25 μ g of ozone in the impingers was very short. Impinger samples indicated much lower ozone concentrations, ranging from 0.131 ppm to 0.541 ppm. Percent agreement for sample sets 6-10 ranged from only 9.9% to 15.4%, and the mean agreement was 11.9%.

Results obtained during MIG welding suggested that conditions or other contaminants present created a negative interference in the AKI procedure. Measurement of NO₂ revealed levels as high as 1.0 ppm. However, the presence of NO₂ did not reduce measured ozone concentrations since it has been shown to create a small positive interference in AKI samples. Because of the higher sampling rate, the pre-filter ahead of the impinger samples did collect more fume than the AID pre-filter for nine of the ten sampling runs. Consequently, catalytic reduction of ozone by welding fume may have been more of a factor for the impinger samples. Fume amounts collected were all below 0.5 mg and therefore the small difference in fume weights for the sample pairs was felt to have a negligible effect. The possible presence of reducing gases such as sulfur dioxide and hydrogen sulfide

was not investigated. These gases would have caused serious negative interferences in the AKI procedure. The problems associated with using the AKI procedure during MIG welding should be studied in more detail.

Conclusions

The AKI procedure seemed to give very low estimations of the true ozone concentration during MIG welding. Since the method is widely used, it is possible that many times in the past, worker exposure to ozone during MIG welding has been a problem that was not documented. Strong consideration should be given to reevaluation of the AKI procedure's validity when used in various industrial situations. The AID Model 560 chemiluminescent ozone analyzer performed extremely well when sampling during MIG welding. Direct-reading ozone monitors should prove to be useful and accurate field instruments for future industrial hygiene applications.

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24 May 1982; Revised 3 January 1983