



Project Summary

Evaluation of Ozone Calibration Procedures

Kenneth A. Rehme, John C. Puzak, Michael E. Beard, C. Frederick Smith, and
Richard J. Paur

Four candidate calibration procedures for the determination of photochemical oxidants in the atmosphere were considered promising replacements for the one-percent neutral buffered potassium iodide (NBKI) procedure in use at the time this project was undertaken: ultraviolet (UV) photometry, gas phase titration with excess nitric oxide (GPT-NO), gas phase titration with excess ozone (GPT-O₃), and an improved potassium iodide technique using a boric acid buffered potassium iodide reagent (BAKI). Each of these procedures had demonstrated results of adequate precision and accuracy under ideal conditions.

All candidate procedures were evaluated to review the procedural descriptions and to assess critical performance parameters. Variability studies were then conducted to estimate the precision and accuracy of the calibrations. The information was used to assess the relative performance of each procedure for calibrating O₃ reference methods.

The reproducibility of a given method, defined as the 95 percent confidence interval of the difference in the slopes of two calibrations performed by different operators using different calibration systems on different days, was also estimated for each of the four methods.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, to announce key

findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

On October 6, 1976, in the Federal Register, the U.S. Environmental Protection Agency (EPA) published an advance rulemaking proposal, citing evidence that the calibration procedure previously specified for EPA reference methods for the determination of photochemical oxidants in the atmosphere was subject to significant error and variability. The notice stated EPA's intention to evaluate alternative calibration procedures prior to proposing amendments to replace or revise the existing procedure.

Four candidate procedures were considered promising replacements for the one-percent neutral buffered potassium iodide (NBKI) procedure then currently in use: ultraviolet (UV) photometry, gas phase titration with excess nitric oxide (GPT-NO), gas phase titration with excess ozone (GPT-O₃), and an improved potassium iodide technique using a boric acid buffered potassium iodide reagent (BAKI). Each of these procedures had demonstrated results of adequate precision and accuracy under ideal conditions.

Each of the candidate procedures was evaluated by an internal EPA working group with members from the Environmental Monitoring Systems Laboratory (EMSL) and the Environmental Sciences Research Laboratory (ESRL) both in Research Triangle Park (RTP), North Carolina. All preliminary procedures were

evaluated to review the procedural descriptions and to assess critical performance parameters. Variability studies were then conducted to estimate the precision and accuracy of the calibrations. The information was used to assess the relative performance of each procedure for calibrating O₃ reference methods.

The variability studies were conducted using volunteers selected from within EPA and outside of EPA to represent technicians likely to use the procedures. Volunteers were provided with a description of the method and asked to familiarize themselves with the procedure and the apparatus. The volunteers were brought to a test laboratory where they generated O₃ concentration standards which were quantitatively compared to a highly stable reference system consisting of three chemiluminescence O₃ analyzers, a UV photometer, an O₃ generation and dilution system, and a dynamic AC line voltage regulator. In the case of the GPT methods, volunteers also generated O₃ concentration standards with a control GPT system in order to estimate the operator contribution to the total variability of these methods.

A least squares linear regression equation was determined for each set of O₃ atmospheres generated. Each regression equation was in the form of:

$O_3 (\text{Volunteer}) = B_1 O_3 (\text{Reference}) + B_2$
An analysis of variance was then performed on the regression slopes to estimate the precision (variability) and accuracy (bias) of each of the methods. The total variability (σ_{tot}) for a given method was broken into two parts: a random component (σ_r) and a calibration system component (σ_c). Random variability is that component of the total variability attributable to chance (experimental error). Calibration system variability is that component attributable to differences in the calibration systems (equipment and operator).

Also estimated for each of the four methods was the reproducibility of a given method, defined as the 95-percent-confidence interval of the difference in the slopes of two calibrations performed by different operators using different calibration systems on different days.

Conclusions

Preliminary Investigations

The preliminary investigation of the UV photometric calibration procedure demonstrated that the technique can be

used to make accurate, highly precise determinations of O₃ in calibration atmospheres. The photometric procedure agreed with an independent method of O₃ analysis, GPT-NO, and with other photometric instruments maintained by independent laboratories. Commercially available O₃ analyzers, based on UV photometry, were found to be suitable for use as primary calibration photometers, provided minor modifications were made. Photometric instruments were stable over long periods of time and could be transported without adversely affecting their reliability.

The procedural parameters and specifications prescribed in the GPT-NO calibration procedure to insure quantitative reaction of O₃ with NO were verified and found to be adequate. The experimental results confirmed that for every molecule of NO consumed during the GPT, an NO₂ molecule was produced. Nitrogen dioxide generated by GPT was essentially equivalent to NO₂ generated by an independent standard, an NBS-SRM NO₂ permeation device. Ozone concentrations assayed by GPT-NO were found to be approximately 8 percent higher than simultaneous assays by UV photometry. Reasons for this discrepancy could not be established; thus, the accuracy of the GPT-NO procedure for O₃ calibrations may be questionable.

Investigation of the procedural parameters and specifications prescribed in the GPT-O₃ calibration demonstrated a potential problem associated with accurately adjusting the GPT conditions (reactant concentrations and residence time in GPT reaction chamber) and a general variability associated with different GPT calibration equipment. Ozone assays using the prescribed procedure were found to be 3 to 6 percent higher than

simultaneous assays by UV photometry. The amount of NO₂ produced during these assays agreed to within 2 percent of the NO consumed, indicating that the observed biases were not caused by O₃ reaction with NO₂. The results of this investigation indicated that the accuracy of the GPT-O₃ procedure for O₃ calibrations may be questionable.

An investigation of the BAKI calibration procedure revealed generally good agreement (± 5 percent) with the UV photometric procedure. A subsequent ruggedness test indicated a potential problem related to O₃ and/or I₂ demands by certain batches of BAKI absorbing reagent. Pretreatment of the absorbing reagent with dilute hydrogen peroxide solution satisfied this demand. The BAKI procedure was revised to incorporate a H₂O₂ treatment step to eliminate this problem.

Variability Studies

The variability of the UV photometric calibration procedure was investigated using five volunteers. Each volunteer operated two commercially available instruments — one in a field monitor configuration and one in a modified configuration (photometer). At the conclusion of the study, each UV instrument (monitor and photometer) was compared to a 2-meter laboratory UV photometer maintained and operated by EMSL, RTP. The results of this variability study are summarized in Table 1.

The results of the analysis of variance for all 10 UV systems indicated a random variability of about ± 0.3 percent of the mean slope. The calibration system variability was about ± 1.2 percent and was statistically significant. Thus, UV calibration systems can lead to biased O₃ calibrations, but the magnitude of the

Table 1. Variability of UV Photometric Ozone Calibrations

System	N*	Mean slope	σ_r	σ_c	σ_{tot}^{**}	Reproducibility
UV	10	1.0037	0.0033	0.0118	0.0123	0.0341
UV monitors	5	1.0110	0.0042	0.0114	0.0121	0.0335
UV photometers	5	0.9964	0.0022	0.0072	0.0075	0.0208
UV corrected	10	1.0052	0.0033	0.0073	0.0080	0.0222
UV monitors corrected	5	1.0059	0.0042	0.0063	0.0076	0.0211
UV photometers corrected	5	1.0045	0.0022	0.0091	0.0094	0.0261

*N = number of UV calibration systems

** $\sigma_{\text{tot}} = \sqrt{\sigma_r^2 + \sigma_c^2}$

variability these biases introduce was less than ± 3 percent of the mean slope. The mean slope for O_3 calibrations using the 10 UV photometric systems showed no bias with respect to the reference system. UV instruments operated in a photometer configuration were less variable than those operated in the field monitor configuration. Referencing the latter UV systems to a central UV photometer reduced the variability to the level exhibited by the UV photometers.

Reproducibility for UV photometric calibrations using the 10 UV systems was ≤ 3.5 percent of the mean slope. Using instruments in the photometer configuration or referencing instruments in the monitor configuration to a central UV photometer reduced the reproducibility to ≤ 2 percent of the mean slope.

Because of the good agreement between the UV photometric calibrations and the reference system, the UV photometric procedure would be a satisfactory independent calibration procedure for reference methods for the determination of O_3 concentrations in the atmosphere.

The variability of the GPT-NO and GPT- O_3 calibration procedures was investigated using ten volunteers. Each volunteer performed O_3 calibrations using a GPT system that he furnished for the study and a common or control GPT system. The control GPT system was used to estimate the operator contribution to the overall variability of the methods. Flow measurements during calibrations using the volunteer GPT systems were referenced to a common flow standard. The volunteer-supplied NO standards were tested by comparison to NBS-SRM's at the conclusion of the studies. These supplemental measurements allowed for estimation of their contribution to the overall variability of the GPT methods. The results of these variability studies are summarized in Table 2 (GPT-NO) and Table 3 (GPT- O_3). The results of one volunteer in the GPT- O_3 study were discarded from the data set because of the large difference in calibration slopes obtained in the replicate runs. The data analysis, therefore, tabulates results for only nine volunteers.

The random components of variability for O_3 calibrations using the volunteer or control GPT-NO systems were the same (about 2 percent of the mean slope). The calibration system component of variability for O_3 calibrations

Table 2. Variability of GPT-NO Ozone Calibrations

System	N*	Mean slope	σ_e	σ_t	σ_{tot}^{**}	Reproducibility
Control	10	1.0315	0.0212	0.0000	0.0212	0.0588
Volunteer	10	1.0742	0.0213	0.0318	0.0383	0.1062
Corrected volunteer	10	1.0576	0.0196	0.0231	0.0303	0.0840

*N = number of participating volunteers

$$^{**}\sigma_{tot} = \sqrt{\sigma_e^2 + \sigma_t^2}$$

Table 3. Variability of GPT- O_3 Ozone Calibrations

System	N*	Mean slope	σ_e	σ_t	σ_{tot}^{**}	Reproducibility
Control	9	1.0236	0.0106	0.0139	0.0179	0.0496
Volunteer	9	1.0787	0.0354	0.0568	0.0669	0.1854
Corrected	9	1.0880	0.0361	0.0221	0.0423	0.1172

*N = number of participating volunteers

$$^{**}\sigma_{tot} = \sqrt{\sigma_e^2 + \sigma_t^2}$$

using the volunteer GPT-NO systems was statistically significant (3 percent of the mean slope), and indicated that GPT-NO O_3 calibrations exhibit an equipment dependent bias. The calibration system component of variability for O_3 calibrations using the control GPT-NO system was statistically insignificant, demonstrating that operator contributions to the total variability cannot be separated from the random component. Besides the system dependent bias, the mean slope for O_3 calibrations using the volunteer systems was biased 7.5 percent higher than the UV reference system.

Referencing NO cylinder assays and flow standards to a central laboratory can reduce the overall variability of the GPT-NO procedure, but the equipment used for O_3 calibrations will still contribute to the variability.

Reproducibility for O_3 calibrations employing the volunteer GPT-NO systems was ≤ 10.5 percent of the mean slope, and ≤ 6 percent of the mean slope for those using the control system. Referencing NO cylinder assays and flow standards to a central laboratory reduced the reproducibility for the volunteer systems to ~ 8.5 percent of the mean slope.

The results indicated that a GPT-NO calibration system could be assembled that will give reproducible results. These O_3 calibrations differ from UV photometric calibrations by an amount

dependent on the equipment (+1 to +15 percent). While the variability of O_3 calibrations using the GPT-NO procedure was acceptable, when coupled with the mean bias in this study, the GPT-NO procedure would be an unsatisfactory independent calibration procedure for reference methods to determine O_3 concentrations in the atmosphere.

The random component of variability for O_3 calibrations using the control GPT- O_3 system was 1.1 percent of the mean slope compared to 3.5 percent of the mean slope for the volunteer O_3 calibrations.

The calibration system component of variability (5.5 percent of the mean slope) for O_3 calibrations using the volunteer GPT- O_3 systems was statistically significant and showed that GPT calibration systems can lead to biased O_3 calibrations using the control GPT- O_3 system was also statistically significant and showed that operator contributions to the total variability were about 1.5 percent of the calibration slope.

Besides the considerable system-induced variability, the mean slope for O_3 calibrations using the volunteer GPT- O_3 systems was biased 8 percent higher with respect to the UV photometric reference system. The large difference in performance between the control and volunteer GPT- O_3 systems demonstrated that a GPT calibration system can be assembled yielding low variability and differing from UV photo-

metric calibrations by only 2 to 3 percent.

Referencing NO cylinder assays and flow standards to a central laboratory reduced the calibration system component of variability, and left random error as the only statistically significant contribution to the total variability. The total variability for the GPT-O₃ corrected calibrations was still larger than the uncorrected GPT-NO calibrations ($\sigma_{\text{tot}} = 0.0423$ for GPT-O₃ corrected and $\sigma_{\text{tot}} = 0.383$ for GPT-NO uncorrected).

Reproducibility for GPT-O₃ calibrations using the volunteer systems was ≤ 18.5 percent of the mean slope. For calibrations using the control system, it was ≤ 5 percent of the mean slope. Referencing NO cylinder assays and flow standards to a central laboratory reduced the reproducibility for the volunteer systems to ≤ 11.5 percent of the mean slope.

These results indicated that the design and construction of the GPT calibrators in use today must be improved. With the large variability and mean bias shown in this study, the GPT-O₃ procedure would be an unsatisfactory independent calibration procedure for reference methods for the determination of O₃ concentrations in the atmosphere.

The variability of the BAKI calibration procedure was investigated using ten volunteers — seven participating at EMSL, RTP, and three participating at laboratories located outside of North Carolina. For the RTP tests, the volunteers furnished the BAKI calibration equipment but were provided with the necessary reagents from a variety of commercial suppliers. The three out-of-state volunteers were required to furnish both equipment and reagents. Volunteer flow measurements during calibrations at RTP were referenced to a common flow standard to estimate their contribution to the overall variability of the method. The results of this variability study are summarized in Table 4. Three of the RTP volunteers were asked to return for additional tests after their initial participation in the study. Since each of these additional tests were conducted under experimental conditions somewhat different than during the volunteers' initial participation, they were treated as separate and not replicate runs.

The random component of variability for O₃ calibrations using the volunteer BAKI systems was approximately ± 2 percent of the mean slope. The calibra-

tion system component of variability (± 5 percent of the mean slope) for O₃ calibrations using the volunteer BAKI systems was statistically significant and showed that BAKI calibrations are subject to significant system-dependent biases. Since no control system was used in the study, operator effects could not be separated from equipment and reagent effects. However, the mean slope for O₃ calibrations using the volunteer BAKI systems showed no bias with respect to the UV photometric reference system.

Referencing flow measurements to a common standard resulted in no significant difference in either the random or calibration system components of variability. The BAKI (corrected) data in Table 4 represents RTP volunteer data with correction for the I₂ molar absorptivity. If the I₂ molar absorptivity was assumed to be 25,600 l mole⁻¹cm⁻¹ instead of being determined by each volunteer during the preparation of the calibration curve, the calibration system variability was slightly reduced.

With the large system-dependent variability shown in this study, the BAKI procedure would be an unsatisfactory independent calibration procedure for reference methods for the determination of O₃ concentrations in the atmosphere.

Recommendations

The results from the preliminary investigations indicated that all four calibration procedures were suitable for the calibration of O₃ reference methods; thus, all four procedures were subjected to further evaluation in variability studies.

The results from the four variability studies are summarized in Table 5. These data indicated that the UV photometric calibration procedures (reproducibility 3.4 percent), and that UV photometers employed for calibration purposes have no significant bias (mean slope 1.0037). The estimated bias value for the UV photometers does not of itself confirm the accuracy of UV photometry, since the reference system for this particular study was also based on UV photometry. However, its accuracy for measuring O₃ concentrations is confirmed by its direct relationship to a well established O₃ absorption co-efficient as well as comparisons of independent UV photometers that showed agreement within ± 1.5 percent.

Accordingly, the UV photometry procedure has been proposed and promulgated by EPA as the replacement for the NBKI procedure for the calibration of O₃ reference methods. Independent use of the BAKI procedure for the direct calibration of O₃ reference methods was

Table 4. Variability of BAKI Ozone Calibrations

System	N*	Mean slope	σ_e	σ_t	σ_{tot}^{**}	Reproducibility
Total BAKI	12	0.9865	0.0216	0.0513	0.0557	0.1544
BAKI	9	0.9769	0.0175	0.0563	0.0590	0.1635
BAKI corrected	9	0.9906	0.0177	0.0415	0.0451	0.1250

*N = number of participating volunteers

$$^{**}\sigma_{\text{tot}} = \sqrt{\sigma_e^2 + \sigma_t^2}$$

Table 5. Comparison of Ozone Calibration Variability

Procedure	N*	Mean slope	σ_{tot}	Reproducibility
UV photometry	10	1.0037	0.0123	0.0341
GPT-NO	10	1.0742	0.0383	0.1062
GPT-O ₃	9	1.0787	0.0669	0.1854
BAKI	12	0.9865	0.0557	0.1544

*N = number of participating volunteers

allowed for an 18-month transition period to permit agencies to adopt the new UV calibration procedure. The use of transfer standards was also allowed, provided they meet certain performance specifications and are certified against the UV photometric procedure. Transfer standards for O₃ can include procedural techniques such as BAKI and the GPT procedures evaluated in this study, as well as devices such as O₃ analyzers and stable O₃ generators.

*The EPA authors **Kenneth A. Rehme, John C. Puzak, Michael E. Beard, and C. Frederick Smith** are with the Environmental Monitoring Systems Laboratory, and **Richard J. Paur** is with the Environmental Sciences Research Laboratory, Research Triangle Park, NC 27711.*

***Kenneth A. Rehme** is the EPA Project Officer (see below).*

The complete report, entitled "Evaluation of Ozone Calibration Procedures," (Order No. PB 81-118 911; Cost: \$18.50, subject to change) will be available only from:

*National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650*

*The EPA Project Officer can be contacted at:
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711*