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AUTOMATED ATOMIC ABSORPTION
DETERMINATION OF LEAD IN GASOLINE

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INTRODUCTION

The determination of lead in gasoline by atomic absorption spectro-
metry has been adopted by the American Society for Testing Materials [1]
and the Environmental Protection Agency [2] as the standard method of
analysis. The method consists of the manual preparation of an in-situ
reaction of the alkyl lead compounds in gasoline with iodine, stabilization
of the alkyl lead iodide complexes with tricapryl methyl ammonium chloride
(Aliquot 336), ten-fold dilution with methyl isobutyl ketone (MIBK) and
measurement by atomic absorption spectrometry with an air-acetylene flame.
The iodine reaction eliminates the problem of variations in response due to
different alkyl lead compounds, Kashiki et al. [3]. The dilution compen-
sates for severe non-atomic absorption, scatter from unburned carbon, and
minimizes matrix effects, Lukasiewiez et al. [4].

The Environmental Protection Agency has initiated a yearly nationwide
survey to determine the extent of pollution control device tampering on
automobiles. Another purpose of these surveys is to determine if fuel
switching has occured, i.e., leaded gasoline is being used in automobiles
designed for use of unleaded gasoline (<0.05 g Pb/gal). Consequently,
these surveys require the analysis of numerous gasoline samples' lead con-
tent within our laboratory. This demand necessitates accurate, rapid
analyses by use of an automated method.

Heistand et al. [5] automated a nitric acid extraction atomic absorp-
tion method for the analysis of lead in gasoline. They stated that the
standard method could not be automated because pump tubing deteriorates

rapidly in the presence of MIBK. The data we generate must be legally defensible and must be comparable with data gathered by the manual standard method. Hence, Heistand's automated method was deemed inappropriate for our application.

The automation of the standard method is discussed below. The incompatability of the MIBK with the pump tubing was initially circumvented by the use of solvent displacement flasks and later by use of constant flow syringe pumps. Data showing equivalence of the automated and manual procedures and precision and accuracy data gathered over a 4 month period during the analysis of about 1,500 samples are presented. The effect of holding times, container types and storage conditions on the lead content of gasoline samples was also studied. Findings indicate a definite need to specify these as requisites in the standard method.

EXPERIMENTAL

Apparatus

A Technicon Auto Analyzer Sampler and a Pump III were used for the automated system. Standard heating block coils (#157-0225) were used for mixing coils because of the need for good mixing with the high-flow rate. A Perkin-Elmer Model 403 atomic absorption spectrophotometer and a strip chart recorder were the detection system used for the manual and automated procedures.

The solvent displacement flasks are Erlenmeyer flasks fitted with silicone rubber stoppers and glass tubing. Later, Model 220 Sage constant-flow syringe pumps fitted with 20 mℓ Teflon-coated syringes were utilized for the addition of MIBK. The solvents are transported through Teflon tubing fitted to the glass with heat shrinkable Teflon tubing. The glassware employed in the manifold is interconnected with polyethylene tubing because tygon tubing dissolved in the presence of MIBK. Solvaflex tubing was found to be compatible with the gasoline. However, the iodine reagent solvaflex pump tubing had to be changed daily.

Reagents

Working standards of lead alkyls in reference fuel (U.S., EPA, RTP, N.C.) were utilized in both procedures. For the manual procedures the iodine solution (Fisher Sci. Co., Fairlawn, NJ) was 3% w/v in toluene (Burdick & Jackson, Muskegon, MI). The automated procedure iodine solution was 0.24% w/v in toluene. In both procedures the Aliquat 336 (Aldrich Chemical Co., Miswaukee, WI), solution was 0.88% in MIBK (Burdick & Jackson, Muskegon, MI). Certified unleaded gasoline was obtained from Phillips Chemical Company, Borger, TX.

PROCEDURE

Manual

The procedure published in the Federal Register [2] was followed except that alkyl lead compounds in isoctane standards were used instead of lead chloride standards.

Automated

The flow diagram of the automated system is illustrated in Figure 1. A sampling rate of 30/hr with a 2:1 sample to wash ratio provides enough peak resolution to establish a baseline at concentrations less than 0.05 g Pb/gal. The procedure screened all samples at a 30/hr sampling rate. Any samples with a lead content greater than 0.05 g/gal were rerun at a sampling rate of 20/hr with a 3:1 sample to wash ratio. The wash solution was certified unleaded gasoline. The sample was diluted and mixed in the first mixing coil with MIBK displaced from a 2-liter flask with distilled water. The iodine reagent (0.24% w/v) was then reacted with the air segmented stream in the second mixing coil. At the flow rates given in Figure 1, the reaction time of the iodine before the addition of the Aliquot 336 was a little over 1 minute. The Aliquot 336 solution was introduced into the system by means of displacement from a 500 ml flask using distilled water. The air segmented stream was then debubbled by reverse displacement and the products of the reaction were pumped into the atomic absorption spectrophotometer. The operating conditions of the Atomic Absorption Spectrophotometer were as follows: wavelength, 283.3 nm; acetylene flow, 20 mℓ/min; airflow, 65 mℓ/min; nebulizer flow, 5.2 mℓ/min.

Sample Storage Study

Containers made of polyethylene, tin with soldered seams, and tin with pressed seams were used in a sample storage study. In addition, tin containers with pressed seams were employed with and without a tin cap insert.

Seven aliquots of the composite sample were analyzed to determine the zero day lead content. Forty-eight 50-mil aliquots were transferred on the same day to the individual sample containers. At intervals of 1, 2, 4 and 23 weeks, three samples of each container type stored at 4°C or at ambient temperature (six samples/container type/interval) were allowed to come to room temperature and then analyzed with the automated system. Subsequently, a similar study was performed with glass containers utilizing a 2-gallon composite test sample.

RESULTS AND DISCUSSION

Manual and Automated Comparison

The additions of the individual reagents of the automated system were designed to match as close as possible those of the manual method. Table 1 shows the volume of each reagent required by the manual method to the volumes of reagents utilized in 1 minute by the automated method. Iodine at a concentration of 3% w/v caused the pump tubing to harden very quickly. The iodine was diluted and its pump flow rate was increased to result in an equal molar concentration addition. The percent total volume and molar concentration of each reagent is very closely matched in both methods.

The comparability between two methods of analysis is usually measured by defining the sensitivity, precision, and accuracy of each method. Four-point calibration curves were prepared over the concentration range of 0.010 g/gal to 0.110 g/gal for both methods. A least squares fit of the calibration data for the manual and automated methods resulted in slopes of

9.8 and 9.1 Abs. Units/g Pb/gal and intercepts of -0.016 and -0.012 respectively. This demonstrates that both systems have about the same sensitivity.

The percent relative standard deviation (% RSD) of replicate analysis of a sample is a measure of the precision of the method. Table II shows the results of the replicate analysis of three samples by the automated method and the replicate analysis of one sample by the manual method. A comparison of the % RSD of the respective methods indicates that the precision is very similar. Another measure of precision can be obtained by the absolute difference of duplicate analysis. Four samples analyzed in duplicate by both methods resulted in the data presented in Table II. The average difference for duplicate analysis by both methods is less than 0.005 g/gal which is the maximum acceptable difference allowed by the standard method. In consideration of these measures of precision, the precisions of both methods are about the same.

The accuracy of both methods was assessed by measuring the lead content of three NBS certified gasoline standards. The results of these analyses are given in Table II. The manual analysis average deviation was slightly biased high, 2.4% ± 7.2%, while the automated analyses are biased low, -3.7% ± 1.8%. Absolute deviations would indicate that since the automated analyses fell within 5% of the true value while the manual analyses were within 10%, the accuracy of the automated method is slightly better than the manual method.

Seventeen unleaded gasoline samples were analyzed by both methods. The results of these analyses are given in Table III. A statistical student T method comparison test indicates there is no statistical difference between the results of the two methods.

There are a number of practical considerations that favor the use of the automated analysis in our laboratory situation. When a workload of 20 samples is on hand, the automated analysis results in a 300% savings in the cost of labor and reagents over manual analysis. In 1-man day, at least 100 sample analyses can be performed by the automated analysis while, in consideration of glassware cleaning, sample preparation and analysis, only about 25 sample analyses can be performed by the manual analysis. The ease with which quality control data can be gathered with the automated analysis offers an advantage that is of uppermost importance in producing legally defensible analyses. An additional advantage of the automated system is that since the entire system is closed, MIBK vapors are cut substantially in the laboratory.

Survey Sample Analysis

Our in-house use of the automated procedure places a heavy emphasis on quality control. This procedure requires first a check of the slope of the calibration curve. All calibration curves used for sample analyses agreed to within 10% of the slope stated earlier. Every tenth sample was analyzed in duplicate. At least one NBS reference standard and at least one blind RTP reference standard was analyzed during an analysis run. All samples with a peak height greater than the 0.05 g/gal standard were rerun and

spiked with known quantities of alkyl lead compounds. Samples were diluted if necessary with unleaded gasoline so that the resulting diluted value, as well as the diluted spike sample valve, fell on the calibration curve.

The quality control results of the analysis of 1,491 samples are sum-marized in Table IV. The average difference of the duplicate analyses very closely approximate zero which would be expected statistically. Within a 95% confidence interval all duplicate analyses performed with the automated system would differ by less than 0.0046 g/gal which is within the accept-able limit of 0.005 g/gal difference established in the standard method. The accuracy of the method evaluated over an extensive period is quite good. Within a 95% confidence interval, values reported over 0.05 g/gal are within 10% of the true value. Values reported below 0.05 g/gal are within 15% of the true value. As indicated by the spiking data, no sub-stantial matrix effects were encountered in the analyses.

The percentage of unleaded gasoline-designed automobiles that switched to leaded gasoline are summarized by state for the 1979 Eight State Survey in Table V. The average fuel switching percentage was 9.3%. The differ-ence between the Vermont I and II studies is that the Vermont II study pop-ulation included a higher percentage of automobiles owned by rural persons.

Sample Storage Study

Polyethylene containers, tin containers with a lead solder seam, tin containers with a pressed seam, tin containers with pressed seams with a stainless steel insert, glass containers with linear polyethylene liners,

and glass containers with Teflon liners were evaluated as to their effects on the lead content of composite gasoline samples. Containers were stored at 4°C and ambient temperature and analyzed at various periods of time. Table VI summarizes the results of this investigation. The values reported are an average of the analysis of three individual samples. The initial lead content of the composition gasoline samples were 0.056 ± 0.014 g Pb/gal for all the containers except glass, and 0.058 ± 0.006 g Pb/gal for the glass containers. Initial values are based on seven analyses. At the end of 1 and 2 weeks, the lead concentrations remained within the initial value ranges. The polyethylene sample container stored at ambient temperatures start to show a concentrating effect at the fourth week. The worst case is the polyethylene container stored at ambient temperatures while the best is the glass container. The concentrating effect is the loss of the lighter weight gasoline fraction. Emission of these vapors is readily detected by the odor emitted from the polyethylene containers.

The results of this study illustrate vividly the need for storage time and types of containers to be specified in the standard method. This is important to assure legally defensible analyses. In consideration of the results presented in Table VI, all samples should be collected in glass containers and analyzed within 4 weeks. Within this time frame, little difference is observed between storage at 4°C and ambient temperatures.

References

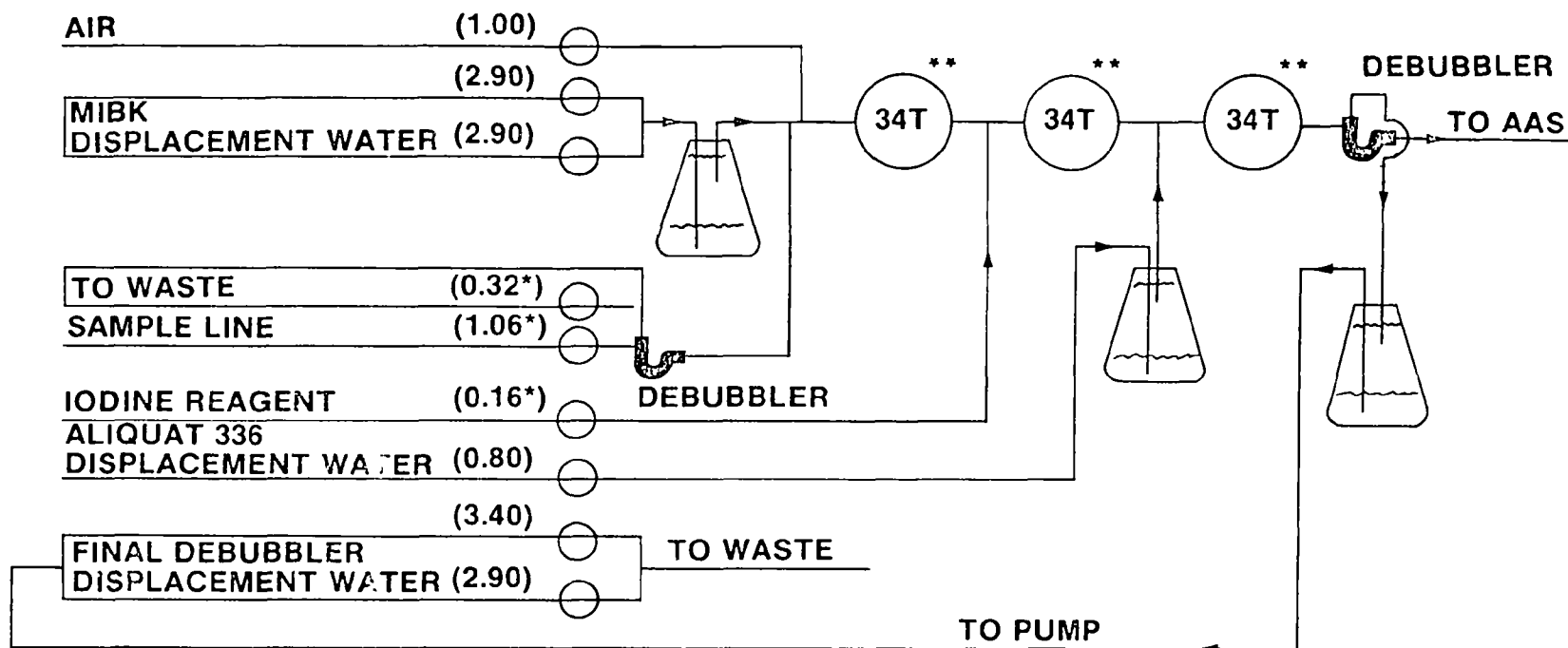1. "Am. Soc. for Testing Materials", Part 17, 1973. Method D 3237, ASTM, 1916 Race Street, Philadelphia, PA 19103.

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AIR   (1.00) ◯
                             (2.90) ◯
MIBK
DISPLACEMENT WATER (2.90) ◯   **   **   **   DEBUBBLER

                                                    34T   34T   34T   TO AAS

TO WASTE   (0.32*) ◯
SAMPLE LINE   (1.06*) ◯

IODINE REAGENT   (0.16*) ◯   DEBUBBLER
ALIQUAT 336
DISPLACEMENT WATER (0.80) ◯

                  (3.40) ◯
FINAL DEBUBBLER   TO WASTE
DISPLACEMENT WATER (2.90) ◯

                                     TO PUMP

Reagent Proportions

Manual		Reagent	Automated	
mL Used	% Total Volume		mL Used*	% Total Volume
39 9	79 8	MIBK	5 80	77 3
5 0	10 0	Std or Sample	0 74	9 9
0 1	0 2	I_2/Toluene	0 16	2 1*
5 0	10 0	1% Aliquot 336/MIBK	0 80	10 7
50 0	100 0	Total Volume	7 50	100 0

*⁺ Concentration of I_2/Toluene solutions are 3% for manual method, 0 24% for automated method

*ML utilized in one minute.

PRECISION

Replicate Analysis

No. of Analyses	Method	Concentration g Pb/gal	% RSD
5	Manual	0.054	3.6
5	Automated	0.010	4.2
5	Automated	0.048	3.5
5	Automated	0.085	3.3

Duplicate Analysis

Sample No.	Automated Avg.	Automated Difference	Manual Avg.	Manual Difference
1	0.031	0.003	0.033	0.001
2	0.043	0.000	0.045	0.002
3	0.012	0.004	0.015	0.001
4	0.101	0.003	0.098	0.008

$$\overline{X}_d = 0.0025 \qquad \overline{X}_d = 0.0030$$

$$S_d = 0.0017 \qquad S_d = 0.0034$$

ACCURACY

NBS Reference Standards

NBS Value g Pb/gal	Automated Value g Pb/gal	Automated % Deviation	Manual Value g Pb/gal	Manual % Deviation
0.0322	0.0307	-4.7	0.0350	+8.7
0.0519	0.0494	-4.8	0.0539	+3.9
0.0725	0.0713	-1.7	0.0685	-5.5

Sample #	Found Value g/gal		Auto-Manual Difference
	Manual	Automated	
1	0 032	0 032	0 000
2	0 044	0 043	-0 001
3	0 014	0 014	0 000
4	0 094	0 099	+0 005
5	0 035	0 034	-0 001
6	0 053	0 052	-0 001
7	0 012	0 007	-0 005
8	0 032	0 032	0 000
9	0 014	1 010	-0 004
10	0 086	0 092	+0 006
11	0 055	0 058	+0 003
12	0 032	0 030	-0 002
13	0 012	0 007	-0 005
14	0 050	0 055	+0 005
15	0 074	0 073	-0 001
16	0 010	0 005	-0 005
17	0 089	0 097	+0 008

$$\bar{x}_{difference} = 0\ 000\ 12$$

$$\delta_{difference} = 0\ 004$$

$$n = 17$$

$$t = \frac{\bar{x}}{\delta} \sqrt{\eta} = 0\ 123$$

For $n-1 = 16$, $t_{05} = 1.746$

Precision
Duplicate Analyses

n	Average Difference, g Pb/gal.	Std Deviation
156	0 00011	0 0023

Accuracy
NBS Reference Stds

n	Concentration, g Pb/gal	Avg % Deviation	Std Deviation
21	0.0322	3.4	6 4
36	0.0519	0.7	4 8
20	0.0725	0.7	4.9

"Blind" Reference Stds.

n	Average Difference	Std. Deviation
23	-0 0009	0 004

Spiked Samples

n	Average % Recovery	Std. Deviation
108	101	5 6

Samples Analyzed   1491

State	Percent
Tennessee	9.7
Delaware	1 9
Minnesota	7 2
Vermont I	15 2
New Jersey	1.6
Texas	10 4
Vermont II	29.1
Virginia	6 0
Arizona	2 2
Average	9 3

TABLE VI

The Effect of Time on the Lead Content of Gasoline Samples with Temperature and Container Type

CONTAINER TYPE

Time Period (wks)	Polyethylene Refrigerated/Ambient	Soldered Seam Refrigerated/Ambient	Pressed Seam Refrigerated/Ambient	Pressed Seam w/Insert Refrigerated/Ambient	Glass w/LPE Liner Refrigerated/Ambient	Glass w/Teflon Liner Refrigerated/Ambient
1	0.057±0.009/0.059±0.002	0.051±0.010/0.063±0.002	0.054±0.007/0.059±0.002	0.060±0.002/0.061±0.006	0.059±0.003/0.058±0.000	0.059±0.006/0.057±0.006
2	0.058±0.012/0.065±0.007	0.061±0.008/0.063±0.011	0.057±0.006/0.065±0.009	0.060±0.007/0.063±0.006	0.058±0.012/0.056±0.018	0.057±0.012/0.058±0.012
4	0.061±0.006/0.076±0.007	0.058±0.012/0.069±0.005	0.053±0.003/0.060±0.005	0.055±0.003/0.065±0.006	0.058±0.006/0.059±0.012	0.058±0.003/0.057±0.003
23	0.100±0.007/0.156±0.003	0.087±0.009/0.093±0.017	0.073±0.005/0.078±0.020	0.092±0.022/0.084±0.002	0.061±0.002/0.061±0.002	0.057±0.003/0.057±0.004

Values are averages for three samples ± three standard deviations; g Pb/gal.
Initial Lead Content: 0.056±0.014 g Pb/gal. for all but glass containers which was 0.058±0.006 g Pb/gal.