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A COMPARISON OF THREE METHODS FOR THE DETERMINATION OF WEAR MET--ETC(U)
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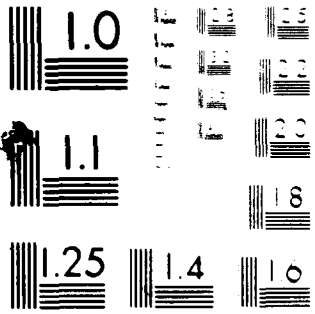
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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER
31

2. GOVT ACCESSION NO.
AD-A113468

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
A Comparison of Three Methods for the Determination of Weal Metals in Lubricating Oils: Direct Introduction-ICP, Solvent Dilution-AAS, and Ashing-AAS

5. TYPE OF REPORT & PERIOD COVERED
Interim

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
J. D. Algeo and M. B. Denton

8. CONTRACT OR GRANT NUMBER(s)
N00014-75-C-0513

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Department of Chemistry
University of Arizona
Tucson, Arizona 85721

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
NR 051-549

11. CONTROLLING OFFICE NAME AND ADDRESS
Office of Naval Research
Arlington, Virginia 22217

12. REPORT DATE
January 20, 1982

13. NUMBER OF PAGES
16

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)

15. SECURITY CLASS. (of this report)
Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

DTIC
ELECTE
APR 15 1982
S D
D

18. SUPPLEMENTARY NOTES

Prepared for publication in Analytical Chemistry.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Wear Metal Analysis, Oil Analysis Nebulizer Technique

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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S/N 0102-LF-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

OFFICE OF NAVAL RESEARCH

Contract N00014-75-C-0513

Task No. NR-051-549

TECHNICAL REPORT NO. 31

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by

J. D. Algeo and M. B. Denton

Department of Chemistry
University of Arizona
Tucson, Arizona 85721

Prepared for Publication
in
Analytical Chemistry

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A Comparison of Three Methods for the Determination of Weal Metals in Lubricating Oils: Direct Introduction-ICP, Solvent Dilution-AAS, and Ashing-AAS

J. D. Algeo[*] and M. B. Denton[†]

Department of Chemistry
University of Arizona
Tucson, Arizona 85721

[*] Present Address: Applied Research Laboratories, 9545 Wentworth St.,
Sunland CA 91040

[†] Author to Whom Correspondence should be Addressed.

Brief

A new method for the analysis of wear metals in lubricating oils which utilizes a modified Babington Principle nebulizer is compared to two other existing methods. The new method is found to be faster and more convenient than the others. When compared to the results from an existing solvent dilution method, the results from the new method show a stronger correlation to those of a reference method.

Abstract

Studies are presented comparing three methods for determination of metals in used lubricating oils. Results of analyses of a series of used oils by direct introduction into an inductively coupled plasma (ICP), by introduction of solvent diluted samples into an atomic absorption spectrophotometer (AAS), and by ashing prior to AAS are presented. The direct introduction method produced results which were more precise than those of the solvent dilution method and also more closely correlated to the values obtained by ashing the samples. The direct introduction method offers greater speed and less opportunity for analyst error.

Introduction

The determination of metals in oils is useful in maintenence programs for oil lubricated equipment (1-6). Although rotating electrode spark source spectroscopy (7) is currently favored because of its multielement capability, there is interest in developing methods based upon the Inductively Coupled Plasma (ICP) and upon Atomic Absorption Spectrophotometry (AAS)(6). Multielement detection of metals in oils by ICP has been reported (8, 9).

The direct analysis of oils by ICP or AAS is complicated by the nature of the samples. Lubricating oils have higher viscosities than samples normally aspirated into plasmas or flames. In addition, the viscosity of a used oil may vary considerably from its original value, with the final viscosity being either higher or lower than the initial viscosity, depending upon the type of oil, operating conditions, and length of service (10). A suitable analytical system should be capable of handling samples of high and variable viscosity without clogging or experiencing changes in sensitivity.

The samples contain particulate matter (1, 2, 4, 11-13) which may cause clogging of the nebulizers commonly used with atomic absorption and ICP spectrophotometers, as well as low recovery of analytes which reside in the particulate fraction.

Previous studies (14) have indicated that a method for the analysis of used oils based upon a novel modification of the Babington Principle nebulizer should be feasible. This method is faster and more convenient than existing ICP-based methods, and should be adaptable to AAS as well. In this paper, studies will be presented demonstrating the use of this approach for the analysis of used lubricating oils. The applicability of the new method is evaluated by comparing it to two methods similar to those developed by Burrows, Heerdt, and Willis (1): solvent dilution-AAS and ashing-AAS. The ashing method, which is insensitive to particulates and varying sample viscosity, is considered a reference method, and the performances of the three techniques are evaluated based on the results of iron determinations in a series of samples obtained from automobile crankcases.

EXPERIMENTAL

Equipment

Details of the nebulizer and sample heater are given in Ref. 14. The ICP system was locally constructed, comprising a 3-tube torch with an extended coolant tube driven at 27.12 MHz, a 0.35 m monochromator, and a computer for system control and data acquisition (15, 16). Samples were delivered to the nebulizer by a stepper motor driven syringe pump which used disposable syringes.

A Varian (Palo Alto, CA) model AA-475 spectrophotometer was used for the AAS analyses.

Sampling

Ten samples of used oil were obtained from automobile engines. These samples are described in Table I. Samples 1, 4, 6, 7, 8, 9 and 10 were taken from hot engines directly into 60 cc syringes. Samples 2 and 5 were from oil drained during regular changes. Sample 3 was taken by syringe from the top of the crankcase of a supercharged small block Chevrolet racing engine which had not been run for one month. Following the sampling, the car was used for several acceleration tests, and sample 4 was then withdrawn from the thoroughly mixed oil by syringe. The oil from which samples 3 and 4 were taken was the first oil used in the engine since a complete overhaul had been performed. During the break-in period of a new engine, the oil may be expected to contain a large amount of metal particulates.

Standards covering the range from 0 to 150 µg/g were prepared by dilution of Conostan (Ponca City, OK) iron standard in Conostan 245 base oil. The recommended level of Conostan stabilizer was added. The standards were stirred for 20 minutes with gentle heating and were allowed to cool overnight before use.

Samples were collected in 60 cc disposable syringes (Model 560S-R, Monoject, St. Louis, MO) and were manually shaken immediately before being placed on the pump.

Samples and standards were injected into the nebulizer and ICP operating under the conditions given in Table II. Results were computed from a linear calibration curve, and all analyses were preformed in duplicate.

Solvent Dilution-AAS

The samples and standards used for the direct introduction work were diluted 1:10 w:w with 4-methyl 2-pentanone (MIBK) and analyzed in an air-acetylene flame, following the procedure outlined by Burrows (1). The manufacturer's recommended operating conditions were used, except that the fuel flow was reduced to compensate for the flammable solvent. All samples were shaken vigorously prior to aspiration and were agitated during aspiration. The assays were carried out in duplicate.

Ashing-AAS

The samples were shaken, and 3 g portions were weighed into porcelain dishes. The samples were then ashed overnight at 550°C. The residues were dissolved in 5 ml portions of concentrated HCl, heated to a boil, transferred to 100 ml volumetric flasks, and brought to volume with deionized water.

Standards were prepared by dilution of a 1000 μg/ml stock solution with deionized water, and contained 5 ml of concentrated HCl per 100 ml of final volume.

The assays were carried out in duplicate using the manufacturer's recommended operating conditions for iron analysis in the air-acetylene flame.

RESULTS AND DISCUSSION

A summary of the results of this method comparison is presented in Table III. The dry ashing produced the highest results. While the solvent dilution method occasionally produced higher values than did the direct introduction method, the direct method was higher in general, producing values which, on the average, were 61% of the dry ashed data, whereas the solvent dilution method yielded, on the average, 52% of the dry ashed results. These differences between methods were all statistically significant ($p < 0.05$).

It was expected that the dry ashing method should produce the highest results, since it is not as sensitive to particle size or matrix interference as are the other two techniques. Assuming that the dry ash data are good estimates of the true amounts of iron in the samples, some interesting observations may be made from a graph of the concentration found by each method (Figure 1).

First, samples 3 and 4 provide a warning about sampling technique. Since these were both taken from the same engine only minutes apart, it is reasonable to assume that the total amount of iron contained in the engine oil is nearly equal in both cases. Sample 3, taken after an opportunity for particulates to settle, gives a much lower concentration than does sample 4, which was taken from a well-agitated crankcase. Since the state of repair of the engine is the same for both samples, this illustrates that a poorly taken sample could give a false confidence that a failing engine was in good repair. Samples should be taken from warm engines, preferably while the engine is running so that the oil circulation will keep the oil well mixed.

Second, all three methods appear to respond to trends in similar fashion. As the concentration found by the ashing method increases, so, in general, do those found by both the solvent dilution and direct introduction methods. The correlation coefficient between the solvent dilution and ashing methods is 0.85. The direct introduction technique is better correlated to the ashing method, attaining a coefficient of 0.96. This correlation is important, since trends in the accumulation of foreign materials in the oils may be useful for diagnosis of engine conditions even if the absolute levels detected are somewhat inaccurate.

The lower correlation figure for the solvent dilution method is accompanied by a high degree of scatter in the results. The mean square due to replication is 744 for the dolvent dilution technique, and 0.2 for the direct introduction method. The poor precision of the solvent dilution technique is likely due in part to the difficulty of maintaining a homogenous suspension of particulates in the low viscosity organic solvent. A visible accumulation of sludge forms at the bottom of the sample bottle when a solvent diluted sample is allowed to stand for about two minutes after having been shaken and analyzed.

The rate of settling of a sphere of radius r and density d in a liquid of density d_0 and viscosity v is given by (17):

$$dx/dt = 2r^2(d-d_0)g/9v \qquad (1)$$

Since the room temperature viscosities of motor oils are typically 200 to 400 times the viscosity of MIBK, and the densities are similar, the settling rate of particulates is much lower in undiluted oil, and a homogenous suspension will persist longer after mixing.

The low values returned by the direct introduction and the solvent dilution methods for sample 4 (a newly rebuilt very high performance racing engine in which recently moved cylinder walls are rapidly wearing to achieve proper ring seating) may be attributed to a failure to accurately measure iron present in metal particles in this particulate laden sample. The solvent dilution method was especially poor with this sample. Sample 5, also from a recently overhauled high performance engine, gave similar results.

CONCLUSIONS

An adaptation of the Babington Principle nebulizer which uses a sample heater to improve efficiency and to minimize viscosity effects has been used to analyze used motor oils without sample pretreatment. A sample may be drawn into, transported in, and analyzed from a single disposable syringe, minimizing handling and eliminating cleanup.

Compared to methods which use dilution in an organic solvent to achieve efficient nebulization and freedom from viscosity effects, the new method offers greater speed, less opportunity for analyst error, and a stronger correlation to the more tedious reference method (ashing-AAS). The method should be adaptable to multielement analyses with appropriate direct reader-ICP equipment. Sample consumption is low, typically 3 to 5 ml per assay.

ACKNOWLEDGEMENTS

This work was partially supported by the Office of Naval Research and by an Alfred P. Sloan Foundation Fellowship to M. B. Denton.

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TABLE I

Description of Motor Oil Samples

SAMPLE NO	OIL BRAND AND SAE GRADE	TYPE OF AUTOMOBILE	MILES ON ENGINE	MILES ON OIL
1	Castrol GTX 20W-50	Fiat	23,900	5,300
2	Amsoil 10W-40	Honda	26,000	6,100
3	Pennzoil HD 30W	Race Car	200	200[a]
4	Pennzoil HD 30W	Race Car	202	202[b]
5	Havoline 10W-40	Corvette	2,800	2,300
6	Castrol GTX 20W-50	Fiat	21,900	3,300
7	Pennzoil 10W-40	Dodge	59,000	6,000
8	Pennzoil 30W	Toyota	42,000	3,000
9	ARCO Graphite	Pontiac	3,100	60
10	Quaker State 10W-30	Chevette	3,500	3,000

a/Cold engine after sitting 30 days

b/Hot engine

TABLE II

ICP SYSTEM OPERATING CONDITIONS

Frequency	27.12 MHz
R. F. Power	2 kW
Coolant Argon Flow	19L/min
Plasma Argon Flow	2L/min
Sample Argon Flow	1L/min
Nebulizer Pressure	30psi
Oil Inlet Temperature	75°C
Sample Flowrate	1.3ml/min
Observation Height Above Load Coil	3cm
Analytical Wavelength	259.9nm
Background Correction Wavelength	260.2nm

TABLE III

METHOD COMPARISON SUMMARY

SAMPLE ID	Fe Concentration Found, ng/g DIRECT INJ.	SOLVENT DIL.	ASHED
1	32	28	52
2	160	164	243
3	87	78	123
4	156	100	322
5	56	36	106
6	23	17	38
7	150	113	208
8	9	11	13
9	32	37	63
10	55	58	75

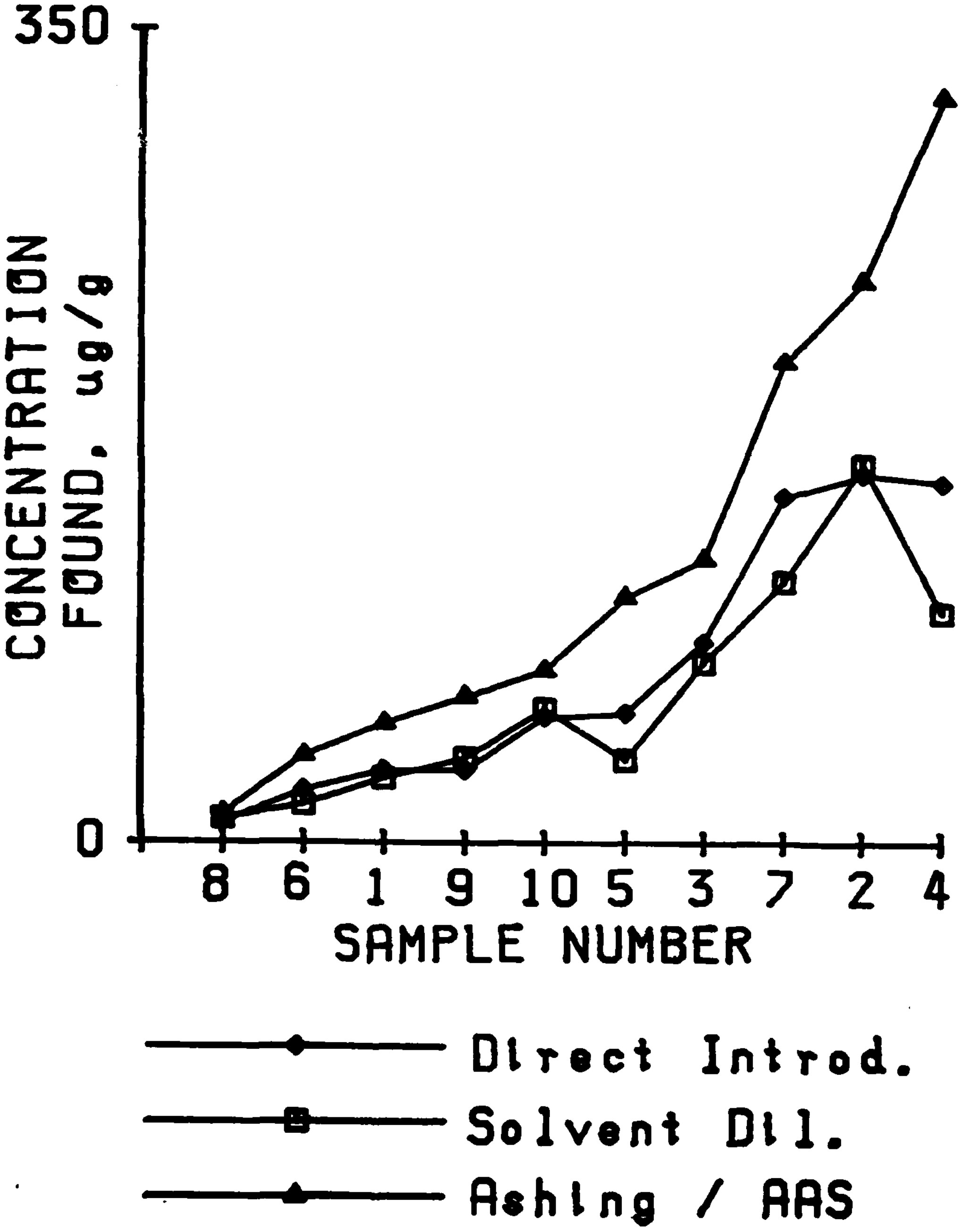
FIGURE CAPTIONS

Figure 1 Concentrations found in 10 Oil Samples by Three Methods:

—◇— Direct Injection

—□— Solvent Dilution

—△— Ashing-AAS


350
0
CONCENTRATION
FOUND, ug/g
8
6
1
9
10
5
3
7
2
4
SAMPLE NUMBER
Direct Introd.
Solvent Dil.
Ashing / AAS

DATE
ILME