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**ATOMIC ABSORPTION TECHNIQUES FOR DETERMINING
VANADIUM AND NICKEL IN CRUDE OIL**

By

P. L. Grizzle, C. A. Wilson, E. P. Ferrero,
and H. J. Coleman

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ATOMIC ABSORPTION TECHNIQUES FOR DETERMINING VANADIUM AND NICKEL IN CRUDE OIL

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P. L. Grizzle¹, C. A. Wilson¹, E. P. Ferrero², and H. J. Coleman³

ABSTRACT

Since trace-metal quantitative data are useful for oil identification, they have been incorporated into the oil-identification research program at the Energy Research and Development Administration (ERDA) Energy Research Center in Bartlesville, OK. (BERC). To improve the reliability of such data further for identifying oils, four different techniques for sample preparation were evaluated for determining vanadium and nickel in crude oils by atomic absorption (AA) spectroscopy: 1. The flame-analyzed dilution method which consists of direct-flame AA analysis after diluting the sample with a suitable organic solvent; 2. the flame-analyzed, wet-ashing method in which the sample is combusted and the residue is then dissolved before flame analysis; 3. the flameless, dilution method which involves flameless AA analysis of the sample following dilution with a suitable organic solvent; and 4. the direct, flameless method in which the crude oil or residue is directly analyzed by flameless AA. The flame-analyzed dilution method yielded erratic and inaccurate analytical results for samples of crude oils as well as for a residual sample containing standard amounts of vanadium and nickel; hence, it is unsatisfactory for oil-identification. Similarly, the direct, flameless method is unsatisfactory owing to the small concentration range available for analysis (less than approximately 15 ppm). Both the flame-analyzed, wet-ashing and flameless-dilution methods yield reliable and reproducible (better than 10 percent) quantitative data for nickel and vanadium in crude oils and crude oil residues. Results demonstrate that the error associated with the loss of volatile metal containing compounds upon wet-ashing is within the reproducibility of the technique. Although wet ashing may be slightly more reproducible,

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the flameless-dilution method is much simpler and faster and is recommended as the better of the two procedures for routine determinations of trace metals for oil identification.

INTRODUCTION

With a continuing increase in the importation of crude oil and, hence, an increase in the number of oil spills, the improvement of existing methodologies and the development and application of new analytical techniques for oil identification are extremely important. Since no single analytical method has been developed for characterization and, hence, identification of each crude oil and related material, a multianalytical approach is required (1,5,16)⁴. Trace elemental analysis and, in particular, trace metal analyses are commonly used in this approach (1,5,8,16).

Vanadium and nickel are among the most abundant trace metals found in crude oils. Quantities of vanadium vary from less than 1 ppm to several hundred ppm, and concentrations of nickel range from less than 1 to more than 100 ppm in crude oils (15). Owing to this large variation of metal concentrations among oil samples and to the small variation in the vanadium-to-nickel ratio upon weathering of an oil sample (1,11,16), quantification of these two metals in crude oils and crude oil residues is useful for oil identification.

Atomic absorption spectroscopy is one of the more common techniques for quantitative trace metal analysis. However, for crude oil and crude oil residue samples, the precision of such analysis is strongly dependent upon the method of sample preparation and introduction. Although the dilution of the oil sample with a suitable solvent followed by flame AA analysis, has yielded good quantitative data for refined products such as lubricating oils and fuel oils (6,14), its specific use with widely varying samples of unrefined oils has not been reported. Alternatively, samples prepared by a conventional wet-ashing technique (3) and analyzed by flame AA have provided good quantitative data (16). Recent studies indicate that quantities of iron, copper, nickel, and manganese can be rapidly and conveniently determined for crude oils by dissolving the oil sample in a suitable solvent followed by subsequent flameless AA analysis (8).

This study evaluated and compared the data obtained by various techniques for analysis of nickel and vanadium in crude oils and crude oil residues with emphasis on precision and reproducibility. Included in the study are analyses for crude oils, residual oils (crude oils topped to 420° C), and an oil obtained from the National Bureau of Standards (NBS) containing certified standard amounts of vanadium and nickel.

⁴ Underlined numbers in parentheses refer to items listed in the references at the end of this report.

EXPERIMENTAL

Flame-Analyzed Dilution Method

For each oil analyzed, three samples were prepared in either methylisobutyl ketone, xylene, or 1-methylnaphthalene. For one sample, a weighed quantity of oil was dissolved in the most suitable solvent before direct flame analysis. The other two samples were prepared by dissolving weighed quantities of the oil sample and Conostan metallo-organic standard obtained from the Continental Oil Co. containing a known concentration (10 ppm g/g) of the metal being analyzed. Measurements were made on a Perkin-Elmer model 403 AA spectrophotometer⁵, and an air/acetylene flame in the absorbance mode was used. Optimum flame and instrumental adjustments were made daily with standard solutions of 10 ppm vanadium and 5 ppm nickel. To minimize matrix interferences (variations in absorbances due to fluctuations in atomization or aspiration of samples arising from difference in solution viscosities), measurements were made with the method of standard additions (7). From the absorbance data for the three samples, actual metal concentrations in ppm (g/g) for each oil were determined by calculating the intercept by use of a linear-least-squares analysis on the concentration axis of a standard addition versus absorbance curve.

Flame-Analyzed Wet-Ashing Method

Samples were ashed by the benzenesulfonic acid method (3,13). Approximately 20 g of oil sample was weighed into a crucible, and approximately 4 ml of a 20-percent solution of benzenesulfonic acid in butanol was added. The resultant mixture was ignited and burned, and the remaining carbon residue was reduced to ash in a muffle furnace at 540° C. The ash was dissolved in hydrochloric acid and quantitatively transferred to a volumetric flask. Final aqueous solutions contained 4 vol-pct hydrochloric acid and 80 ppm potassium chloride as a buffer. Standard solutions were prepared to span the expected concentration range and to match the sample matrix in percent hydrochloric acid and buffer solution. Using these standard solutions, flame and instrumental adjustments were made to obtain direct concentration readout on the model 403.

Flameless-Dilution Method

Measurements were made with an Instrumentations Laboratory (IL) model 251 AA spectrophotometer equipped with an IL model 455 flameless furnace and programmable calculator (Tektronix model 31). For both nickel and vanadium determinations, furnace-operating conditions included a drying cycle (10 sec @ 75° C and 10 sec @ 225° C), charring cycle (20 sec @ 750° C and 20 sec @ 1200° C) and atomization cycle (5 sec @ 3000° C). For all determinations, argon (9.4 l/min) was used as the purge gas.

⁵ Reference to specific brands of equipment is made for identification only and does not imply endorsement by ERDA.

Calibration curves based upon absorbance peak heights and areas (integration time, 3 sec) were obtained by use of the programmable calculator by measuring the absorbances of five standard solutions. Standards were prepared by dissolving a weighed quantity of Conostan metallo-organic standard, containing 10 ppm of nickel or of vanadium in tetrahydrofuran (approximately 10 ml). For nickel and vanadium determinations, concentrations of the standard solutions extended from approximately 20 to 200 ppb and 40 to 350 ppb, respectively.

Oil samples were prepared for analysis by dissolving a weighed quantity of crude oil or residue in tetrahydrofuran (approximately 10 ml). All samples were introduced into the graphite cuvette with a 10 μ l Eppendorf pipett. Using the programmable calculator and stored calibration curves, concentrations of nickel and of vanadium in the tetrahydrofuran solution were determined directly. Assuming the density of the standard and analyzed oil solutions to be the same, concentrations (g/g) were calculated.

Direct Flameless Method

Measurements were made with the IL model 251 as previously described. Furnace operating conditions for both nickel and vanadium determinations included a drying cycle (5 sec @ 75° C and 5 sec @ 225° C), charring cycle (30 sec @ 750° C and 30 sec @ 1200° C), and atomization cycle (5 sec @ 3000° C). Argon (11.8 l/min) was used as the purge gas.

Calibration curves based upon absorbance peak heights and areas (integration time, 3 sec) were obtained by measuring the absorbances of five standard samples. Standard samples were prepared by weighing various quantities (approximately 1 to 4 mg) of Conostan oil containing a known concentration of either nickel or vanadium onto a graphite microplate. For both nickel and vanadium the weight of each metal in the standard samples varied from approximately 1-10 ng.

Oil samples were analyzed similarly by weighing 1 to 5 mg of oil onto the microplate. Using the programmable calculator and stored calibration curves, quantities (ng) of nickel or vanadium were determined directly and the concentrations (g/g) calculated.

RESULTS AND DISCUSSION

Flame-Analyzed Dilution Method

The sample dilution technique represents a convenient method of sample preparation for flame AA analysis because of its simplicity and speed. This technique has been used successfully with refined products such as lubricating oils and fuel oils (6, 14) and was, therefore, tested on crude oils and residual oils.

For flame AA analysis, three organic solvents were investigated for use as diluents with crude oil and residual samples. The first solvent examined, methylisobutyl ketone, was not satisfactory because it would not completely dissolve highly viscous residual oils. The second solvent, xylene, was more satisfactory for high viscosity oils, but would not completely dissolve highly paraffinic oils. A third solvent, 1-methylnaphthalene, was studied, but it did not dissolve the highly paraffinic oils as well as did the xylene. Of the three solvents, xylene was selected as the most desirable solvent for the types of oil samples in this study, and it was subsequently used for all flame AA determinations made with the sample dilution method.

Table 1 presents nickel and vanadium concentrations (average of three determinations) and associated standard deviations for a select group of oil samples, as determined by the flame-analyzed dilution method. As seen by the magnitude of the deviations, the results

TABLE 1. - Vanadium and nickel concentrations in selected crude oils¹
determined by flame-analyzed dilution and
flame-analyzed wet-ashing methods

Sample Number	Field and State	Vanadium, ppm		Nickel, ppm	
		Dilution	Wet-ash	Dilution	Wet-ash
73012	Village Mills East, Texas ²	2.9±5.0	0.1±0.0	0.4±0.2	0.5±0.0
73014	Village Mills East, Texas ²	2.6±4.6	.1±0.0	3.5±4.1	.6±0.0
73015	Village Mills East, Texas ²	3.0±5.2	.2±0.1	3.8±4.7	.6±0.0
73016	Kismet Northwest, Kansas	17.4±6.2	17.2±0.1	7.9±2.7	6.6±0.1
73019	Earlsboro, Oklahoma	6.5±6.9	2.4±0.1	7.7±3.4	1.4±0.1
73020	Ship Shoal, Louisiana	.2±0.4	.4±0.1	3.0±2.6	.9±0.0
73022	Sooner Trend, Oklahoma	4.2±5.0	1.1±0.1	7.3±9.5	.4±0.1
73031	Sunoco Felda, Florida	42.0	45.5±2.5	70.5	45.9±1.6
73055	Gillisburg, Mississippi	1.2±0.4	.1±0.1	4.7±2.1	.4±0.4

¹ Samples were chosen from a group of more than 230 crude oils and residua (crude oil topped to 420° C) which were analyzed for vanadium and nickel by either or both of the two sample preparation techniques.

² Texas samples are from the same field but from different wells representing different producing zones. Oils 73012, 73014, and 73015 are from the Cockfield, Z; Cockfield, O; and Cockfield, V-Y producing zones, respectively.

are erratic. Several reasons for this are noteworthy, the first of which is the lack of a universal solvent. This is particularly bothersome when solvent dilution causes precipitation of asphaltenes and waxes. Second, large differences in sample viscosity cause

substantial variations in aspiration rate, and although use of a premix burner reduces the effect of aspirator fluctuation (10), this burner did not entirely compensate for the viscosity effect on aspiration. Third, oils which have not been refined may contain some inorganic materials such as water that can cause variation of flame temperatures or aspiration rate. Finally, high concentrations of dissolved solids, as well as undissolved materials that pass through the aspiration tube, often cause the burner head to clog gradually (10) and give erratic results. Although appreciable amounts of suspended material could be removed by filtration before analysis such a procedure could produce substantial errors in the quantities of metals present. Even though the method of standard additions is designed to minimize the previously mentioned interferences, it was not sufficient to compensate for the magnitude of variations that arise with routine crude oil and residuum samples.

Since the results in table 1 show that the reproducibility obtained by the flame-analyzed dilution method is poor, for a small number of determinations, the precision should also be poor. To verify this, an oil containing known concentrations of nickel and vanadium was obtained from the NBS, and a series of dilution determinations was made. Classified by the NBS as a residual oil, this oil was extremely viscous and was, therefore, representative of some of the matrix problems involved with the sample oils studied. The results presented in table 2, show that determinations of nickel and vanadium could not be reproduced within the desired 10 percent accuracy by the flame-analyzed dilution method. For the vanadium and nickel determinations, the relative percent standard deviations are 16.5 and 16.1 percent, respectively, based upon 22 determinations. Naturally, a smaller number of determinations would increase the uncertainty even more. It should be noted that although the concentration of vanadium as determined by the dilution method (82 ppm) is in good agreement with that obtained by the NBS (79 ppm), the average nickel value obtained by the dilution method (119.8 ppm) differs by more than 28 percent from the value supplied by the NBS.

In addition to inconsistent results from separate dilutions, a rerun, made later the same day from a given sample dilution, generally showed a large percentage difference from the earlier run, both for the NBS standard oil and for sample crude oils (table 3). This lack of repeatability from a given dilution eliminated the individual sample preparation as the source of error responsible for such highly erratic results. Since physical properties inherent to the crude oil samples were determined to be the major problem with this method of AA analysis, the flame-analyzed dilution method will not provide reproducible data with the precision required for oil identification.

Flame-Analyzed Wet-Ashing Method

Sample ashing is a more time-consuming, complex procedure than direct sample dilution (2,6), and care must be taken to ensure no loss of volatile metal compounds. Although much of the vanadium and nickel in crude oils exist as metallo-porphyrins or similar type complexes (4,9), the metals can be lost from these complexes in a volatile form as the

TABLE 2. - Repetitive vanadium and nickel determinations on a
standard reference oil¹ by flame-analyzed dilution
and flame-analyzed wet-ashing methods

Vanadium, ppm		Nickel, ppm	
Dilution results	Wet-ashing results	Dilution results	Wet-ashing results
94.3	77.0	118.3	84.4
72.1	78.0	104.5	85.5
108.0	87.9	128.7	90.4
55.6	81.4	140.0	93.0
91.8	79.3	120.7	83.9
72.4	75.6	116.3	87.1
84.8	--	114.5	--
88.8	--	151.3	--
81.9	--	127.0	--
105.4	--	101.9	--
99.5	--	95.5	--
95.7	--	116.3	--
73.8	--	140.3	--
77.4	--	98.9	--
75.7	--	97.1	--
79.9	--	91.4	--
71.4	--	125.6	--
61.4	--	121.4	--
85.2	--	112.7	--
69.5	--	156.6	--
85.2	--	153.6	--
74.1	--	102.2	--
Average 82.0	79.9	119.8	87.4
Standard deviation 13.5	4.4	19.3	3.6
Deviation of average from NBS value, pct 3.8	1.1	28.8	6.0

¹ The standard oil was General Material GM-5, vanadium and nickel in residual oil (specific gravity 1.001 at 60°/60° F) obtained from the Office of Standard Reference Materials, National Bureau of Standards, Washington, D. C. Standard metal contents were vanadium, 79.0 ppm, and nickel, 93.0 ppm, with ± 1.2 standard deviation in both cases.

TABLE 3. - Repetitive determinations of nickel by the flame-analyzed dilution method from the same dilution

Sample Number	Field and State	Nickel, ppm		Percent difference $\frac{R_1 - R_2}{R_1} \times 100$
		Run 1	Run 2	
73014	Village Mills East, Texas ¹	2.1	1.4	33.3
73015	Village Mills East, Texas ¹	1.6	.5	68.8
73016	Kismet Northwest, Kansas	6.7	3.0	55.2
73019	Earlsboro, Oklahoma	3.7	5.4	-45.9
73020	Ship Shoal, Louisiana	1.3	3.1	-138.5
GM-5 ²	NAp	156.6	153.6	1.9
GM-5 ²	NAp	151.3	114.5	24.3
GM-5 ²	NAp	104.5	128.7	-23.2
GM-5 ²	NAp	95.5	125.6	-31.5
GM-5 ²	NAp	91.4	97.1	-6.2
GM-5 ²	NAp	116.3	140.3	-20.6

NAp - Not applicable.

¹ Texas samples are from the same field but from different wells representing different producing zones.

² Standardized oil obtained from the National Bureau of Standards containing 93.0 ppm nickel.

sample burns during ashing. The addition of benzenesulfonic acid has been found to break down these complexes and form nonvolatile, sulfur-linked compounds that can be reduced to an ash without appreciable loss of the metals (2,13).

Since all carbonaceous material was removed by ashing and the sample was made up in an aqueous solution, matrix differences were almost entirely eliminated. Quantitative results were more consistent and more easily duplicated within 10 percent, and standard deviation values were good (table 1). Even though the NBS standard was an extremely difficult sample to analyze because of its high specific gravity and viscosity, the ash method results showed much better agreement with the standard values, and standard deviation values were much lower than those obtained with the flame-analyzed dilution method (table 2). Although more time-consuming than the direct sample dilution method, the data in tables 1 and 2 demonstrate that more accurate, reproducible quantities of nickel and vanadium can be obtained by the wet-ashing method than by the flame-analyzed dilution method.

To verify that volatile metal compounds are not lost during the ashing procedure, several analyses were made using a previously analyzed sample to which known amounts of vanadium and nickel standards were added before the ashing procedure. The theoretical and experimentally determined concentrations of nickel and vanadium and associated percent deviations are given in table 4. On the average, the experimental results for the spiked sample are 6.4 and 6.6 percent lower than the theoretical concentrations of vanadium and nickel, respectively. Note that these values are only slightly larger than the uncertainties in the quantities of nickel (4.1 percent) and vanadium (5.5 percent) obtained from 22 determinations of the NBS standard by the ashing procedure. (See table 2.) Hence, the error introduced by the loss of volatile metal compounds during the ashing procedure is essentially within the limits of reproducibility.

TABLE 4. - Comparison of theoretical and experimental results of a
spiked sample¹ obtained by the flame-analyzed
wet-ashing method

Metal	Theoretical ppm	Experimental ppm	Percent deviation
Vanadium	34.8	32.5	6.6
	52.0	47.7	8.3
	48.1	44.2	8.1
	96.4	93.9	2.6
Nickel	26.1	23.1	11.5
	48.3	45.8	5.2
	47.8	46.1	3.6
	96.1	90.1	6.2

¹ Sample (73022) was a crude oil from Sooner Trend field, Oklahoma, spiked with Conostan metallo-organic standards.

Great care was necessary during ashing, particularly with samples that required large dilutions after ashing to reduce them to the linear working range. These dilutions have the effect of magnifying errors in sample preparation or readout. In spite of this, the results obtained from the ashed samples were far superior to those obtained by the flame-analyzed dilution method.

Flameless-Dilution Method

As previously discussed, the sample dilution technique is convenient for flame AA sample preparation because of its simplicity and speed. Although the results obtained with the flame-analyzed dilution method are not encouraging, the use of a flameless furnace circumvents some of the problems inherently associated with the flame analysis. (See above discussion.)

Two solvents, methylisobutyl ketone and tetrahydrofuran, were investigated as diluents in this latter part of the study. Methylisobutyl ketone with a trace of nitric acid has been previously used for the analysis of nickel in oils, including crudes and fats such as hydrogenated oils (12). Although reasonable data were obtained by use of methylisobutyl ketone for some of the samples studied, crude oil residues and crudes containing waxes are not completely soluble. Considering the small sample sizes introduced into the graphite cuvette, nonhomogeneity of the solution will produce inaccurate, non-reproducible data. The use of tetrahydrofuran was suggested by the spectrophotometer manufacturer. For the samples investigated, tetrahydrofuran is superior to methylisobutyl ketone as a solvent, and unlike methylisobutyl ketone (12), oil solutions in tetrahydrofuran containing nickel and vanadium in concentrations of 100 to 400 ppb are stable for several hours.

Table 5 presents nickel and vanadium concentration (average of three determinations) data and associated standard deviations for a select group of oil samples, as determined by both the flame-analyzed wet-ashing method and the flameless-dilution method. For the samples studied, the uncertainties in the nickel and vanadium concentrations are approximately 10 percent. For the nickel determinations, concentrations determined by the ashing and dilution procedures are in much better agreement than those obtained by the flame-analyzed dilution procedure. (See table 1.) For the vanadium determinations, the agreement between the ashing and flameless-dilution techniques is reasonable. However, agreement is better for nickel determinations than for vanadium determinations. Since some smoke is evident even in the atomization cycle, the disagreement in the vanadium determinations reflects, in part, the necessity of using a hydrogen background correction lamp. The present study employed the correction lamp in the nickel determinations but not in the vanadium determinations. It is important to note that the detection limit for nickel is lower than that for vanadium using these instrumental conditions and sample preparation procedures.

During this study, difficulties were encountered in obtaining quality graphite cuvettes. Recent metal determinations with new cuvettes show that reproducibility may be even better than that given in table 5. Findings of these investigations, involving many representative worldwide crude oils, and emphasizing the importance of trace metal analysis for oil identification will be published later.

TABLE 5. - Vanadium and nickel concentrations as determined by
flame-analyzed wet-ashing, flameless dilution, and
direct flameless methods

Sample Number	Nickel, ppm			Vanadium, ppm		
	Flame AA	Flameless AA		Flame AA	Flameless AA	
	Wet-ashing	Dilution	Direct	Wet-ashing	Dilution	Direct
73014	0.6	0.26±0.02	0.28±0.01	0.1	ND	0.67±0.23
73016	6.6	8.79±0.98	8.33±0.20	17.2	23.02±1.47	--
73019	1.4	1.16±0.08	1.14±0.05	2.4	2.39±0.31	2.23±0.27
73020	.9	.92±0.05	.62±0.01	.4	ND	.73±0.32
73022	.4	.57±0.02	.50±0.08	1.1	2.30±0.19	1.37±0.16
69074	33.7	36.0 ±1.6	--	ND	--	--
70025	58.2	62.4 ±1.9	--	442.2	507.3 ±20.3	--
71011	8.8	7.73±0.80	8.00±0.40	28.2	21.1 ±20.3	--

ND - Not detectable under the conditions employed.

Direct Flameless Method

The direct determination of nickel and vanadium without prior sample preparation is the most convenient method of analysis. This method requires only a small quantity of sample (typically 1 to 5 mg) and data can be obtained rapidly.

Table 5 presents nickel and vanadium concentration data and associated standard deviations for a select group of oil samples, as determined by the direct-flameless, flame-analyzed wet-ashing, and flameless-dilution methods. For nickel determinations, the agreement between the concentrations obtained by the ashing, flameless-dilution, and direct methods is good. The uncertainties in the concentrations are also quite satisfactory. For the measurements of vanadium concentration, the agreement between the three techniques is also good. However, the uncertainties associated with the average concentrations are higher for vanadium than for nickel. As previously discussed, the increased uncertainty in the vanadium-concentration data results from the absence of the hydrogen correction lamp in the vanadium determinations.

Although the results in table 5 show that reasonable quantitative data can be obtained by the direct-analysis method, the technique does have some disadvantages. First, due to the large amount of smoke produced during both the charring and atomization cycles, the optics must be cleaned several times daily. Without the use of the correction lamp, the calibration curve will not remain valid during the day unless the optics are cleaned frequently. More importantly, for the instrumental conditions used, samples containing

more than approximately 10 to 15 ppm of either nickel or vanadium cannot be analyzed easily by this procedure. For determining nickel and vanadium above these concentrations in crude oil samples, the sample size required for direct-flameless analysis is too small to be easily weighed on a microbalance. Thus, for oil samples containing more than 10 to 15 ppm of either nickel or vanadium, the ashing or flameless-dilution methods must be employed. For this reason, samples 69074 and 70025 and samples 73016, 70025, and 71011 could not be analyzed for nickel and vanadium, respectively, with the direct-flameless procedure.

CONCLUSIONS

Four different techniques were investigated for the analysis of crude oils and crude oil residues for nickel and vanadium by atomic absorption spectroscopy. Although the flame-analyzed dilution method using xylene as an organic solvent was generally simpler and faster than the flame-analyzed wet-ashing procedure, the precision and reproducibility obtainable by the flame-analyzed dilution technique was not satisfactory. The dilution method can be useful for refined petroleum products that have levels of matrix interference low enough for compensation by use of the method of standard additions (6,14), but this method was not satisfactory for unrefined crude oils or residual oils. Matrix effects (caused by such things as suspended solids, water, high-viscosity samples, or undissolved organic or inorganic materials) were too great for compensation by use of the method of standard additions. Thus, the flame-analyzed dilution technique was unsatisfactory for analyzing a general spectrum of crude oils and residual oils.

Alternatively, the procedure for the flame-analyzed wet-ashing method was more detailed and more time-consuming and precautions had to be taken against loss of volatile vanadium and nickel compounds. However, the results indicate that the method yields meaningful data. Ashed sample results could be duplicated from day to day, and expected values were obtained on samples of known vanadium and nickel content.

Although the results obtained using the flame-analyzed dilution method are not satisfactory for oil identification, the use of a flameless furnace circumvents some of the problems inherently associated with the flame analysis. For the samples investigated, tetrahydrofuran was determined to be superior to methylisobutyl ketone in regard to both oil solubility and stability. The concentrations of nickel and vanadium obtained by this procedure are in good agreement with those obtained by the ashing technique. Although the associated uncertainties in the determined quantities of nickel and vanadium are slightly greater than those associated with the ashing determinations, the data are reliable for oil identification.

Of the four methods, the direct determination of nickel and vanadium without prior sample preparation by flameless analysis is the most convenient. For the samples analyzed, the agreement between the metal concentrations obtained by ashing, flameless-dilution, and direct methods is good, and the reproducibility is satisfactory. However, for the

instrumental conditions used, samples containing more than approximately 10 to 15 ppm of either nickel or vanadium cannot be analyzed easily by the direct-flameless procedure. Thus, data suitable for oil identification can be obtained by this technique but only over a small range in metal concentrations. For this reason, the direct technique is unsatisfactory for analyzing a general spectrum of crude oils and residual oils.

Results from this investigation show that the flame-analyzed wet-ashing and flameless-dilution methods yield the more reliable and reproducible quantitative data for nickel and vanadium in crude oils and crude oil residues. Although the ashing method may be more reproducible, the dilution method is much simpler and faster. Approximately 20 to 30 metal determinations can be obtained daily by the flameless-dilution method as compared to only 10 to 15 by the flame-analyzed-wet-ashing technique. Considering all factors, the flameless-dilution method is the better of the two for routine determinations of trace metals for oil identification and has been incorporated into the BERC oil identification program.

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