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Determination of Trace Elements in Lube and Furnace Oil Using Atomic Absorption Spectrophotometric Techniques

Wasim Ahmad[1], Shahnaz Alam[1] and Muhammed Pervaz[1]

ABSTRACT

Estimation of Na, K, Ca, Mg, Ba, Al, Si, Pb, V, Cr, Fe, Ni, Cu and Zn in 100 samples of lube and furnace oils provided by various organizations has been successfully carried out using Atomic Absorption spectrophotometric techniques (AAS). A wet ashing, direct dilution with MIBK (Methylisobutyl Ketone) were applied for the preparation of aspiratory solutions for AAS. The results are comparable to other available techniques both in accuracy and limit of detection. The direct dilution method was abandoned in favour of wet ashing method, due to high operational cost and low reproducibility at lower level of concentration.

INTRODUCTION

The determination of trace elements in samples of petroleum origin is a difficult proposition as most of the elements to be determined are often present in samples as organometallic compounds and may sometimes be present both in organic and inorganic forms. This heterogeneous character of petroleum samples makes the choice of suitable analytical procedure rather difficult and decisively affects the accuracy of the particular determination.

A wet ashing method was developed to carry out the analyses of Na, K, Ca, Mg, Ba, Al, Si, Pb, V, Cr, Fe, Ni, , Cu and Zn in fuel oils, lubricating oils and other petroleum products. These elements are usually present in very low concentration usually in the range of 3 to 15 ug/ml.

The amount of trace elements in petroleum products is used to monitor the wear, tear and corrosion of metal parts (Sprague and Slavin, 1963; Burrows et al., 1965). For example Vanadium and Nickle are important constituents of normal engine alloys and their determination in worn lubricating oils can indicate the condition of engine. similarly large amount of Vanadium in fuel oil indicates the corrosion problems.

Several methods (Wilson and Wilson, 1960, 1962; National Bureau of Standards Monograph, 1962; Bartles and Slater, 1970; Means and Ratcliff, 1965) are used by various workers for the estimation of trace metals in lube /furnace oils but atomic absorption is an ideal technique for such type of samples, and was used in the present study to carry out the estimation of these metals. The methods of analyses vary from direct injection of diluted sample to wet ashing of samples. In direct injection method the samples are diluted with Xylene or MIBK and injected in atomic absorption spectrophotometer. The amount is calculated from standards similarly prepared from organometallic compounds.

The direct injection methods are comparatively less time consuming but are very expensive due to high cost of organometallic compounds. The other disadvantage is that it is pre-requisite that organometallic standards in organic solvents have virtually the same viscosity as that of sample. Otherwise there will be difference in aspiration rate, yielding erroneous results. In view of this (Sprague and Slavin, 1965) a method was developed using technique of wet ashing which yielded satisfactory results.

EXPERIMENTAL

Instrumentation

All measurements were carried out with a Perkin Elmer model 703 atomic absorption spectrophotometer equipped with background corrector and a burner for air-acetylene/nitrous oxide-acetylene flame. A single element hollow cathode lamp was used as the primary light source. Other experimental conditions used are given in Table 1.

Standards

All the stock solutions of standards were prepared from analar grade salts of elements of interest. The working standards were prepared from stock solution by making necessary dilutions.

Sample Preparation

50 to 100 grams of sample is weighed in porcelain dish, added 5 drops of H_2SO_4 and then the sample is evaporated to dryness by slow heating. 10 ml of H_2SO_4

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[1] Hydrocarbon Development Institute of Pakistan, Islamabad.

Table 1. Standard analytical conditions.

Element	Wavelength (n.m)	Analytical line	Slit setting (n.m)	Flame type	Sensitivity (u.g/ml for 1 % A)	Remarks
Na	589.0	295-Vis	4	A/Ac(oxi)	0.015	HCL
K	766.5	383-Vis	4	"	0.040	HCL/EDL
Ca	422.7	211-Vis	4	=	0.080	HCL
Mg	285.2	285-UV	4	=	0.007	HCL
Ba	553.6	277-Vis	2	N/Ac(Red)	0.400	HCL
Si	251.6	252-UV	3	=	1.800	HCL
Pb	283.3	283-UV	4	A/Ac(oxi)	0.500	HCL/EDL
Cr	357.9	358-UV	4	=	0.100	HCL
Ni	232.0	232-UV	3	=	0.150	EDL/HCL
V	318.4	318-UV	4	N/Ac(Red)	1.700	HCL
Cu	324.8	325-UV	4	A/Ac(oxi)	0.090	HCL
Zn	213.9	214-UV	4	=	0.018	HCL/EDL
Al	309.3	309-UV	4	N/AC(Red)	1.000	HCL/EDL
Fe	248.3	248-UV	4	A/Ac(oxi)	0.120	HCL
Ag	328.1	328-UV	4	=	0.060	HCL
Sn	286.3	286-UV	4	N/Ac(Red)	4.100	HCL

HCL= Hollow Cathode Lamp
EDL= Electrodeless Discharge Lamp
A/AC (oxi)= Air-Acetylene Oxidizing
N/Ac (Red)= N2O-Acetylene Reducing

Table 2. Trace elements in petroleum samples determined by wet ashing techniques.

Lab. No.	Total Ash %	Fe %	K %	Na %	Ca %	V %	SiO2 %	Insoluble %	Volatile matter %
1.	98.1	2.0	0.83	14.5	0.76	8.3	1.30	0.06	1.9
2.	98.7	1.8	1.04	24.1	0.67	7.1	0.92	0.6	1.3
3.	97.6	2.0	0.83	13.7	0.86	8.7	1.64	0.39	2.4
4.	99.7	1.0	0.83	29.0	0.76	1.3	1.31	6.68	0.3
5.	99.5	3.0	0.83	23.7	0.86	3.9	2.50	6.15	0.5
6.	99.4	0.9	1.04	26.2	0.96	2.2	1.87	4.65	0.6
7.	99.4	1.4	1.04	24.0	0.86	1.4	1.57	8.49	0.6
8.	99.2	1.4	1.04	24.2	0.76	1.5	2.20	8.0	0.8
9.	99.4	1.6	1.04	27.7	0.67	1.4	1.90	7.86	0.6
10.	97.2	2.6	1.04	20.2	0.86	10.6	1.84	1.61	2.8
11.	97.8	2.1	0.83	16.3	1.92	7.6	1.30	0.31	2.2

Lab. No.	Cu PPM	Zn PPM	Ca PPM	Mg PPM	Fe PPM	Pb PPM	Si PPM
1.	5.95	404.60	2567.56	69.34	323.74	1.25	
2.	0.21	446.40	2364.84	78.46	8.81	1.25	162.00
3.	0.56	001.21	1106.41	118.61	4.49	2.81	63.00
4.	0.26	646.90	0031.75	456.56	6.65	12.17	
5.	58.69	490.20	2820.94	401.44	683.45	11.85	18.00
6.	0.43	842.76	2635.13	781.02	4.58	0.62	
7.	0.30	817.00	1199.32	768.24	0.62		
9.	0.21	125.00	1773.64	129.56	4.49	0.62	64.00
10.	0.21	102.57	1182.42	105.84	2.69	26.30	

Table 3. Analytical results for miscellaneous samples in ppm.

Lab No.	Na	K	Ca	Mg	Ba	Al	Pb	Fe	Ni	V	Cu	Zn
890	–	–	4059	13	–	–	1	–	2	–	–	470
891	–	–	34	1270	–	–	4		–	2	–	781
892	–	–	159	–	–	–	–	–	–	–	697	
893	–	–	104	1465	–	–	5	–	1	–	–	917
894	2	–	–	–	–	–	14	3	26 –	–	–	
895	5	2	–	–	–	–	–	20	9	53	–	
896	5	–	–	–	–	15	1375	197	– –	2	–	
897	6	–	–	–	–	–	14	110	– –	1	–	
898	6	–	–	–	–	11	1375	99	– –	3	–	
899	1	B.D	2	–	–	–	–	–	– –	–	7	
900	1	B.D	3	–	–	–	–	–	– –	–	–	
901	2	B.D	12	–	–	–	–	–	– 21	–	–	
902	–	–	226	–	–	11	645	21	– –	–	–	919
903	–	–	–	–	–	–	–	–	– –	–	–	
904	1	2	1437	2224	–	–	–	221	– –	–	137	
905	2	2	1812	2214	–	–	–	257	– –	–	95	
331	5	–	8	–	–	15	–	–	7 7	–	–	
332	6	–	1	–	–	25	11	1726	4 22	–	–	
306	1	B.D	11	–	475	1	–	3	–	315	1	1
307	236	1	–	–	–	–	–	–	– –	–	–	
634	8234	268	B.D	B.D	B.D	–	–	16	– –	–	B.D	
635	7993	226	B.D	B.D	B.D	–	–	15	– –	–	–	
636	1	B.D	B.D	B.D	B.D	–	–	94	– –	–	1	
A-1	–	–	–	–	21	–	–	160	– 3	–	–	
A-2	–	–	–	–	19	–	–	166	– 2	–	–	
A-3	–	–	–	–	16	–	–	222	– 1	–	–	
B-1	–	–	–	–	15	–	–	109	– 2	–	–	
B-2	–	–	–	–	8	–	–	–	– –	–	–	
C-1	–	–	–	–	5	–	–	88	–	1	–	
C-2	–	–	–	–	5	–	–	42	– B.D	–	–	
C-3	–	–	–	–	B.D	–	–	72	- 1	–	–	
D-1	–	–	–	–	19	–	–	180	– 2	–	–	
D-2	–		–	–	17	–	–	152	– 2	–	–	

Table 4. Analytical results for lube oil samples in ppm.

Lab No.	Zn	Cu	Fe	Pb	Mg	Ca	SiO2
313	1100	52.2	2.0	0.5	70	1200	162
314	1050	53.1	1.9	0.3	401	1100	63
315	1100	55.2	3.5	0.4	781	32	18
401	1100	25.0	4.5	1.2	129	–	64
402	1100	24.0	1.0	0.9	132	25	67
403	1050	23.8	0.86	0.8	136	52	63
405	–	12.2	–	–	–	–	–
425	0330	15.3	1.6	12.0	110	50	24
426	1050	14.2	2.5	11.0	121	52	30
427	1000	0.3	2.3	11.5	123	32	65
450	0315	9.0	0.70	–	22	–	24
451	–	10.0	26.0	–	–	–	–
452	–	3.0	4.0	9.0	8	220	B.D
453	0002	2.0	553.0	B.D	26	203	2600
461	167	0.2	683.0	26.3	129	35	95
462	250	0.4	3.0	24.0	132	41	89
463	520	0.1	7.3	19.2	133	52	75
464	250	0.5	4.5	B.D	134	55	73
465	292	0.6	3.2	B.D	155	58	75
466	416	0.2	3.5	B.D	151	47	81
467	750	5.8	323.0	1.2	73	2567	900
468	576	0.2	8.9	1.2	78	2364	1500
469	306	0.5	5.0	2.8	113	1106	1700
470	292	0.3	7.0	12.1	413	2721	1800
471	625	55.0	650.0	10.2	402	2820	1472
472	963	0.4	4.6	0.7	719	2635	2100
473	1389	0.5	3.8	0.8	752	1199	2203

Table 5. Analytical results of furnace oil samples in ppm.

Lab No.	Na	K	Ca	Pb	V	Fe
723	4	01	3.5	0.02	11	15.6
724	32	01	2.8	0.03	30	14.6
725	29	01	1.6	0.02	53	92.7
726	21	25	3.9	0.05	46	80.2
832	31	268	1.6	0.03	44	47.2
833	20	226	3.5	0.04	32	12.3
834	8	198	3.0	0.03	44	18.1
852	20	155	3.1	0.06	39	29.2
853	11	132	1.6	–	53	25.0
854	27	2	2.9	0.01	51	31.0
855	26	3	2.7	0.03	47	7.2
889	29	6	3.2	0.2	51	8.1
222	12	12	3.3	0.1	42	6.2
223	4	B.D	4.1	0.2	40	0.9
224	4	4	5.0	50.0	18	0.7
225	15	1	4.3	–	–	0.5
226	2	3	1.3	–	–	0.6

is added and again evaporated to dryness (till there are no fumes of H_2SO_4). After that the sample was ignited in muffle furnace at 700°C to make ash.

The sulphated ash was further treated with aqua-regia thrice and evaporated to dryness each time. Finally solution was made with 5% HCl or HNO_3 depending upon the elements of interest. The acid used for dissolution of the ash was also used for making calibration standards.

RESULTS AND DISCUSSION

The type of samples received from the clients varied from light oil to heavy fuel oil. Results of analyses are presented in Tables 2-5. The monitoring of analysis was carried out by the introduction of standard with every batch of samples. For comparison purposes,few samples were also analyzed using direct dilution method (MIBK). Analytical results are presented in Table 3. The viscosity of standards and samples were made identical in order to avoid any discrepancy in aspiration rate. The results obtained by this method are comparable with the ashing method.

Calibration curves were constructed by using standards of appropriate range, usually in the range 1 & 15 PPM. The detection limits were taken twice the standard deviation just above the blank values. The calibration curves for most of the elements were linear in the used range (Table 1).

The method has been found relatively free from interferences and no adverse effect of a hydrocarbon matrix was observed. Calcium and barium showed some interference effect in the air acetylene flame but no such effect was observed in nitrous oxide-acetylene flame. The use of a high temperature flame, however, introduced a potential ionization interference which was overcome by the addition of alkali to supress this effect (Table 2).

The method yielded reproducible results despite of the fact that the lubricating oils which were analyzed differed widely in composition and viscosity (Table 4, 5).

CONCLUSION

The method described herein offers a considerable advantage over direct dilution method and can be routinely used for trace elements analyses in petroleum products. There is virtually no interference between resonance lines of different elements. The method is relatively rapid after sample preparation. By this method relatively higher accuracy and lower limit of detection can be achieved.

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