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ASHING PROCEDURE FOR THE DETERMINATION OF METALS IN PETROLEUM FUELS

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ABSTRACT. A procedure is described for the determination of Ca, Cr, Cu, Fe, Mg, Ni, Pb, and Zn in gasoline and kerosene using sulphanilic acid as asking reagent and igniting the samples during asking. Significant metal level enhancements were achieved with 0.03 g of sulphanilic acid per gram of the fuels because of a corresponding reduction in volatilisation losses. A quicker analysis was achieved through sample ignition which also contributed to reduce volatilisation losses. The procedure is reproducible and comparable in accuracy to other established procedures.

INTRODUCTION

Of the organometallic compounds present in crude oil, the ones associated with Ni, V, Cu, Fe, and As are of major concern to the refiner [1]. Although earlier belief was that all metal bearing compounds remain behind in the residue during distillation, it is known that some of these compounds are carried over into the distillate fractions [2]. Based on the behaviour of V and Ni, about 5% of the total organometallics enter the boiling range of the overhead distillates, kerosene and gasoline [1] and the need to remove these compounds from refined products causes difficulties in the refinery [3]. High concentrations of some inorganic elements in fuels causes corrosion or attacks fuel-burning and power generating equipment [3, 4]; hence, the level of metallic elements in a fuel is an index of its corrosivity [3].

Metal determinations in petroleum oils have relied on asking procedures that prevent metal losses due to volalisation during sample ignition [5-9]. The use of benzene sulphonic acid to destroy the porphyrin metallocomplexes present in an oil and render the metals in volatile has been reported [10]. The losses of volatile porphyrins of Ni and V from petroleum distillates have been prevented by the use of this reagent [11] and the Institute of Petroleum has adopted it as ashing reagent for petroleum samples [12]. An extension of this ashing procedure involving the use of *p*-xylenesulphonic acid as ashing reagent in the determination of Cu, Fe, Ni, and V in fluid catalytic feed stocks has been described [7]. While benzenesulphonic acid and *p*-xylenesulphonic acids are hygroscopic and require special handling and storage [7], sulphanilic acid is stable at room temperature and has been investigated as ashing reagent in this work for the determination of Ca, Cr, Cu, Fe, Mg, Ni, Pb, and Zn in kerosene and gasoline samples.

EXPERIMENTAL

Reagents and apparatus. All reagents used in this work were of analytical reagent grade. Doubly distilled water was used in preparing all aqueous solutions. A Gallenkamp

Tactical 308 Sizel muffle furnace capable of maintaining a constant temperature in the range 25-1200 °C was used in ashing samples. Metal concentrations were determined using a Pye Unicam 919 atomic absorption spectrophotometer equipped with a premix chamber and a single slot burner head, operated on air-acetylene flame.

Preparation of solutions. 1000 ppm stock solutions of Ca, Fe, Mg, Ni, and Zn were prepared as described by Whitehead [13], that of Cr as described by Vogel [14] and those of Cu and Pb as described by Allen *et al.* [15]. Standard solutions for calibration were obtained by appropriate dilution of the stock solutions introducing 5% La as nitrate in the cases of Ca and Mg to contain the interferences of phosphate and other stable oxyanions.

Fuel samples. Gasoline and kerosene samples investigated were either purchased from commercial firms in Zaria, Nigeria or obtained from final product storage tanks of the Kaduna Refinery and Petro-Chemical Company (KRPC), Kaduna, Nigeria as indicated in Table 1.

Table 1. Description of samples.

Sample No.	Sample type	Sample source
1	gasoline	regular station (AP)
2	gasoline	regular station (National)
3	gasoline	private surface storage
4	gasoline	KRPC tank
5	kerosene	regular station (AP)
6	kerosene	regular station (National)
7	kerosene	private surface storage
8	kerosene	KRPC tank

Ashing procedure. 10.0 g of gasoline sample was weighed into a 400 mL Pyrex beaker, 0.3 g of sulphanilic acid was added and the mixture ignited in a fume cupboard and allowed to burn out. 20.0 g more of the sample and 0.6 g of sulphanilic acid were added to the coke, which was ignited again and allowed to burn out as before. This step was repeated with another 20.0 g of the sample and 0.6 g of sulphanic acid to bring the total sample size to 50.0 g. The coke was then charred with a Bunsen flame until it stopped smoking. The beaker and its content was then heated in a muffle furnace at 550 °C (for 2 h) until a carbon-free ash was obtained.

In the case of kerosene sample, 50.0 g of the sample was mixed with 1.5 g of sulphanilic acid in a 400 mL Pyrex beaker. The mixture was heated on a hot plate so that it can support a flame when ignited. The burning and heating were carried out simultaneously until the flame goes out. The coke was charred with a Bunsen flame until smoking ceased as in the case the of gasoline samples. The coke was then heated in a muffle furnace at 550 °C (for 2 h) until a carbon-free ash was obtained.

The carbon-free ash obtained in each case was dissolved in 10.0 mL HCl (50% v/v), digested to obtain a clear solution [16], allowed to cool and made up to 50 mL with water in a volumetric flask. The solutions were analysed for Ca, Cr, Cu, Fe, Mg, Ni, Pb, and Zn by flame atomic absorption spectrometry (FAAS).

RESULTS AND DISCUSSION

Ashing conditions. The muffling temperature of 550 °C was selected as optimum after investigating the range of temperatures 400-650 °C [19]. Carbon-free ash was consistently obtained for both gasoline and kerosene samples by muffling at 550 °C for 2 h.

Effect of amount of sulphanilic acid. The effect of mass of sulphanilic acid on the metal yield were investigated using samples 1 and 5. For each sample, 50.0 g of sample was coked, charred, muffled and the ash solubilised and measured as before without sulphanilic acid and, again, in the presence of varying masses of sulphanilic acid. The results (averages of three determinations) are given in Table 2 and 3. These results show that significantly enhanced levels of all test metals were observed when sulphanilic acid was added as asking agent to samples. This reagent renders the test metals present as in volatile metal sulphanilate and retains them in the coke for analysis. During muffling the sulphanilates are decomposed to metal oxides in the ash. The higher thermodynamic stability of the metal sulphanilates relative to that of the volatile porphyrin analogues is a possible explanation for these results.

Table 2. Effect of mass sulphanilic acid on the release of metals from gasoline.

Mass of sulpanilic acid (g)	Determinant concentration (ppm)				
	Ca	Cr	Fe	Mg	Pb
0	2.72	7.40	1.76	bd	bd
0.2	2.91	8.20	1.78	0.01	bd
0.4	3.29	9.00	2.60	0.01	0.01
0.6	3.94	9.75	3.00	0.01	0.01
0.8	4.61	11.20	3.03	0.02	0.02
1.0	5.21	13.48	3.65	0.02	0.02
1.5	5.20	13.51	3.66	0.02	0.02
2.0	5.22	13.50	3.66	0.02	0.02
2.5	5.21	13.50	3.65	0.02	0.02

bd = below detection.

Table 3. Effect of mass of sulphanilic acid on the release of metals from kerosene.

Mass of sulphanilic acid (g)	Determinant concentration (ppm)						
	Ca	Cr	Fe	Mg	Ni	Pb	Zn
0	2.54	8.76	3.54	bd	bd	bd	0.01
0.2	2.74	9.23	3.87	0.01	bd	bd	0.03
0.4	3.18	10.44	3.92	0.01	bd	bd	0.09
0.6	3.74	11.27	4.04	0.01	bd	bd	0.12
0.8	4.01	13.43	4.16	0.02	bd	bd	0.18
1.0	4.58	14.30	4.21	0.03	0.01	bd	0.25
1.5	5.82	15.23	4.83	0.03	0.01	0.01	0.25
2.0	5.80	15.23	4.81	0.03	0.01	0.01	0.25
2.5	5.82	15.23	4.80	0.03	0.01	0.01	0.25

bd = below detection.

The optimum ratio of sulphanilic acid to fuel was 0.8 g in 50 g of gasoline for Mg and Pb, 1.0 g in 50 g of gasoline for Ca and 1.5 g in 50 g of gasoline for Cr and Fe. The ratio was 1.0 g in 50 g of kerosene for Mg, Ni and Zn but 1.5 g in 50 g of kerosene for Ca, Cr, Fe, and Pb. Bearing in mind the errors, there is no difference in results for all additions of 1.0 g or more (gasoline) and 1.5 g or more (kerosene) within the normal variations in the detection limits for the various analytes. Thus optimum metal release was achieved with 1.5 g of sulphanilic acid for 50 g of sample. Hence 1.5 g of sulphanilic acid was added regularly to 50 g of sample to ensure optimum release of all test metals; this corresponds to 0.03 g of sulphanilic acid per gram of gasoline or kerosene. A blank analysis on 2.0 g of sulphanilic acid indicated undetectable levels of all the test elements; it therefore did not contribute to the test metal result observed.

Effect of ignition. The effects of combustion on the efficiency of metal release were investigated by evaporating 50.0 g of sample 1 (gasoline) to dryness in a 400 mL Pyrex beaker on a hot plate but without igniting the vapour. Alternatively, 50.0 g of sample were ignited at the mouth of the beaker but without simultaneously heating the beaker on a hot plate. In the case of kerosene, 50.0 g of sample 5 were evaporated to dryness in a 400 mL Pyrex beaker by heating on a hot plate either with or without igniting simultaneously the vapour. The coke obtained was in all cases heated on a muffle furnace at 550 °C and the ash solubilised as before and analysed by FAAS. The average optimum results of triplicate analyses are given in Table 4.

The results (Table 4) indicate that ore metal is realised when samples are ignited. The higher metal recovery must result from a reduction in volatilisation losses. Gasoline samples burn out of control if they are simultaneously heated and ignited, hence, they were only ignited for safety considerations. Ignition of samples, with simultaneous heating in the case of kerosene samples, causes a large reduction in coking and analysis time and is recommended.

Table 4. Effect of ignition on the release of metals from gasoline and kerosene.

Sample No.	Treatment	Duration of coking (h)	Determinant concentration (ppm)						
			Ca	Cr	Fe	Mg	Ni	Pb	Zn
1	only heated	36	3.10	10.21	3.01	bd	bd	bd	bd
1	only ignited	1	5.20	13.50	3.65	0.02	bd	0.02	bd
5	only heated	48	3.85	14.60	4.60	0.03	0.01	0.01	0.18
5	heated and ignited	1.5	5.76	17.20	4.80	0.03	0.01	0.01	0.25

bd = below detection.

Precision of the procedure. The reproducibility of the recommended procedure was determined by repeating the asking and analysis six times for each of samples 1 and 5. The results are presented in Table 5. Relative deviations in the range 0 - 4.5% (gasoline) and 0 - 2.3% (kerosene) were obtained which show that the recommended procedure is highly reproducible.

Table 5. Reproducibility of procedure.

Sample No. (type)	Element	Replicate results (ppm)							
		1	2	3	4	5	6	Mean	RSD
1 (gasoline)	Ca	5.3	5.1	5.2	5.2	5.4	5.0	5.2	2.72
	Cr	13.5	13.5	13.3	13.4	13.6	13.5	13.5	0.81
	Fe	3.66	3.96	3.56	3.66	3.46	3.66	3.66	4.57
	Mg	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0
	Pb	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0
5 (kerosine)	Ca	5.6	5.9	5.9	5.9	5.7	5.8	5.8	2.24
	Cr	15.0	15.1	15.3	15.2	15.4	15.2	15.2	0.92
	Fe	4.8	4.8	4.6	4.9	4.9	4.8	4.8	2.29
	Mg	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0
	Ni	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0
	Pb	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0
	Zn	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0

Recovery of added nickel. The recovery of added metal was determined by introducing 5.0, 20.0 and 50.0 ppm of nickel cyclohexane butyrate dissolved in amyl alcohol in 50.0 g of each of samples 4 (gasoline) and 8 (kerosene). The samples were then coked, ashed and the ash dissolve and analysed for Ni by FAAS. The results obtained for triplicate determinations are presented in Table 6. Recoveries of 94-96% were obtained for gasoline and 95-97% for kerosene. These recoveries are good enough to rule out significant matrix effects on the determination of nickel in both matrices by the recommended procedure.

Table 6. Recovery of added nickel.

Sample No. (type)	Ni concentration (ppm)		
	added	detected	Recovery (%)
4 (gasoline)	5.0	4.7	94.0
	20.0	19.2	96.0
	50.0	47.2	94.4
8 (kerosene)	5.0	4.8	96.0
	20.0	19.4	97.0
	50.0	47.6	95.2

Comparability with other procedures. The procedure [17] applied routinely by KRPC laboratory to determine metals in gasoline and kerosene uses 50.0 g of the sample which is evaporated to dryness on a hot plate. The beaker is subsequently heated in a muffle furnace with its content at 550 °C for 1 h. The cooled ash is digested in HCl to a clear solution which is diluted to 50.0 mL with water and analysed by FAAS.

The standard Universal Oil Products (UOP) method 800 [18], wet-ashes the sample with 1.0 mL of fuming H_2SO_4 per gram of sample, the charr is burnt off at 565 °C, the ash is dissolved in 5.0 mL of HCl. The solution is made up to 50.0 mL with water and analysed by FAAS.

Table 7. Comparison of results obtained by three methods.

Sample No.	Element	Concentration (ppm)		
		Present method	UOP method 800 [18]	KRPC procedure [17]
1	Ca	5.20	5.01	1.22
	Cr	13.50	13.83	11.43
	Cu	bd	bd	bd
	Fe	3.66	3.85	0.70
	Mg	0.02	0.03	bd
	Ni	bd	bd	bd
	Pb	0.02	0.04	bd
	Zn	bd	0.01	bd
2	Ca	5.00	5.05	1.34
	Cr	14.42	14.70	11.20
	Cu	bd	bd	bd
	Fe	4.52	4.71	0.80
	Mg	0.03	0.03	bd
	Ni	bd	bd	bd
	Pb	0.02	0.03	bd
	Zn	0.01	0.01	bd
3	Ca	5.62	3.67	2.14
	Cr	16.60	16.85	11.68
	Cu	bd	bd	bd
	Fe	6.40	6.40	1.20
	Mg	0.08	0.08	0.01
	Ni	0.01	0.09	bd
	Pb	0.15	0.18	bd
	Zn	0.50	0.50	bd
4	Ca	4.67	4.69	1.31
	Cr	14.10	14.20	10.63
	Cu	bd	bd	bd
	Fe	3.87	3.98	0.84
	Mg	0.02	0.02	bd
	Ni	bd	bd	bd
	Pb	bd	bd	bd
	Zn	0.25	0.25	bd
5	Ca	5.80	5.82	2.92
	Cr	15.20	17.23	12.85
	Cu	bd	bd	bd
	Fe	4.81	5.14	1.20
	Mg	0.03	0.05	bd
	Ni	0.01	0.01	bd
	Pb	0.01	0.01	bd
	Zn	0.25	0.36	bd
6	Ca	5.61	5.60	2.51
	Cr	16.30	16.85	11.27
	Cu	bd	bd	bd
	Fe	4.87	4.91	1.05
	Mg	0.03	0.04	bd
	Ni	0.01	0.01	bd
	Pb	bd	bd	bd
	Zn	0.18	0.21	bd

Table 7. Cont'd.

7	Ca	6.72	6.85	3.10
	Cr	15.97	16.10	12.61
	Cu	bd	bd	bd
	Fe	7.62	7.50	2.26
	Mg	0.03	0.03	0.01
	Ni	0.02	0.02	bd
	Pb	0.14	0.16	bd
	Zn	0.41	0.50	bd
8	Ca	4.72	4.80	2.10
	Cr	14.21	14.25	10.20
	Cu	bd	bd	bd
	Fe	4.01	4.05	1.31
	Mg	0.02	0.02	bd
	Ni	bd	bd	bd
	Pb	bd	bd	bd
	Zn	0.16	0.16	bd

bd = below detection.

The procedure recommended in this work were compared for the test metals using the KRPC laboratory procedure and the standard UOP method 800. The results obtained are presented in Table 7.

The results obtained for the same samples using the recommended procedure and the standard UOP method 800 (Table 7) were in good agreement. The student t-test showed that, at the 95% confidence level, there was no significant difference between the results of all the determinants listed in Table 7 using either the recommended procedure or the standard UOP method. A linear regression was obtained between determinant results, y, obtained by the standard UOP method and those, x, obtained in the same samples by the recommended procedure. The regression line had the equation $y = 1.028 x - 0.012$ and a regression coefficient $r = 0.9979$.

The student t-test indicated that there was a significant difference at the 95% confidence level between the results obtained by the KRPC laboratory procedure and either the results obtained by the UOP method 800 or those obtained by the recommended procedure. Results obtained by the KRPC laboratory method were generally low for all the determinants in all samples investigated. This difference is expected as the KRPC procedure does not contain any precaution against volatilisation losses. The merit of sulphanilic acid as ashing reagent is reflected in the increased determinant levels; these arise as a result of recovery of metals from their porphyrins to form metal sulphanilates which are retained as such and decomposed to less volatile metal oxides during muffling.

CONCLUSION

The procedure reported is reproducible and yields similar results to other standard procedures. It is simpler and quicker than the UOP method 800.

REFERENCES

1. Petrolite Corporation Laboratories, *Impurities in Petroleum-Occurrence, Analysis, Significance to Refinery and Petrochemical Operations,* Petreco Division, Houston, Texas 77001, 1968.
2. Woodle, R. A.; Chandler, W.B. *Ind. Eng. Chem.* **1952,** 442, 591.
3. Milner, O.I. *Analysis of Petroleum for Trace Elements, International Series of Monographs on Analytical Chemistry,* Vol. 14, Pergamon: Oxford; 1963; p 81.
4. Jones, M.C.K.; Hardy, R.L. *Ind. Eng. Chem.* **1952,** 44, 2615.
5. Karchmer, J.H.; Gunn, E.L. *Anal. Chem.* **1952,** 24, 1733.
6. Gamble, L.W.; Jones, W.H. *Anal. Chem.* **1955,** 27, 1456.
7. Row, W.A.; Yates, K.P. *Anal. Chem.* **1963,** 36, 368.
8. Skorko-Trybula, Z. *Nafta Krakow.* **1966,** 22, 141; *Anal. Abstr.* **1967,** 14 , 5505.
9. Udoh, A. P.; Thomas, S. A.; Ekanem, E.J. *Bull. Chem. Soc. Ethiop.* **1990,** 4, 13.
10. Erdman, J.G.; Shott , J.E.; Garland ,T.J.; Clark, R.O. *Anal. Chem.* **1961,** 33, 506.
11. Shott, J.E. Jr.; Garland, T.J.; Clark, R.O. *Anal. Chem.* **1961,** 33, 506.
12. Institute of Petroleum, *IP Standards for Petroleum and its Products, Part 1: Methods of Analysis and Testing,* 45th ed., Institute of Petroleum: London; 1985, Vol. 1 pp 110.1, 111.1, Vol. 2 pp 286.1, 308.1.
13. Whitehead, P.J.; *Pye Unicam Atomic Absorption Data Book,* Pye Unicam: Cambridge; 1975.
14. Vogel, A.I.; *A Textbook of Quantitative Inorganic Analysis,* 3rd ed., Longmans: London; 1961.
15. Allen, S.E.; Grimshaw, H.M.; Parkinson, J.A.; Quarmby, C. *Chemical Analysis of Ecological Materials,* Black Well: Oxford; 1974; p 178.
16. Udoh, A.P.; Thomas, S.A; Ekanem, E.J. *Talanta* **1992,** 39, 1591.
17. Kaduna Refinery and Petrochemical Company, *Undated Laboratory Manual,* **KRPC:** Kaduna.
18. Universal Oil Products, *Laboratory Test Methods for Petroleum and its Products,* Vol. II, UOP Process Division: Texas; 1979, pp 1-12.
19. Lori, J.A. *Ph.D. Thesis,* Ahmadu Bello University, Nigeria, 1996.