Determination of Trace Metals in Crude Oil Samples by Atomic Absorption Spectroscopy Using a Mixed Solvent System

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Summary: Crude oil samples from various oil fields of Pakistan have been analysed for metal ions by using a mixed solvent system as well as by dry ashing procedure. It has been found possible to eliminate the use of organo-metallic standards hence in both cases pure metals or inorganic salts are used as reference materials. Absorbance of trace metals has been measured in an air-acetylene flame.

Introduction

A knowledge of trace elements in crude oil is essential for the petroleum technologist. The nature of metal constituents and their abundance in crude oil yield valuable information about the origin, migration and maturation of the oil. The information is also helpful in refining process as the metal constituents are responsible for the corrosion of equipment and poisoning of the process catalyst.

Atomic absorption spectroscopy has been successfully employed for the determination of trace metals in crude petroleum and its finished products in the form of additives, injurious impurities and wear metals [1,2]. Two approaches have been generally adopted for this purpose. In first the oil sample is carefully burnt and residue is extracted with an inorganic acid. The extract is then diluted and aspirated into the flame. The dry ashing procedure offers an advantage of using inorganic standards but usually lacks the accuracy of results because of losses during combustion process. In second approach the sample is diluted with a suitable organic solvent and then directly aspirated into the flame. In this method reference materials are organometallic compounds which are essentially soluble in the organic solvent [3,4]. Another problem which usually arises in this approach is that aspiration of pure organic solvent turns the flame opaque and smoky. A number of acid digestion procedures have also been reported after which direct determination against reference solutions is usually recommended [5,6], but most of these procedures are tedious, cumbersome and time consuming.

Present work involves the use of a mixed solvent system and inorganic standards for the determination of trace metals in crude oil samples. The proposed mixture would have four components: a pure organic solvent 5-15% like butan-2-one, to dissolve the organic material, water (5-15% to accomodate the inorganic metal content, hydrochloric

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acid (1-15%) to dissolve or decompose the metal content into aqueous phase and ethanol (30- 55%) as the bulk solvent to blend the other components of the system and to control the flame conditions. This type of mixed solvent has been successfully employed for the determination of tin and antimony in their organo-metallic compounds by flame methods [7,8]. However in present work, to maintain the homogeniety of sample solutions an additional solvent, propan-2- ol has to be added.

A number of oil samples collected from various fields of Pakistan have been analysed for metal ions by the proposed mixed solvent system and results obtained are compared with those obtained by dry ashing procedure.

Experimental

Equipment and Reagents

A Varian-1275 atomic absorption spectrophotometer equipped with standard hallow cathode lamps and a recorder was used for absorption measurements.

Inorganic salts, acids and metals used for calibration standards were of AnalaR Grade. However organic solvents were used without any further purification.

Standard Solution

Calibration standards of silver, copper, iron, nickel, zinc and magnesium were prepared by dissolving the pure metal in minimum quantity of nitric acid and diluting the solution with doublly distilled water. For other metals, oven-dried salts preferably anhydrous nitrate and chlorides were used for preparing the calibration standards. However in case of calcium, anhydrous calcium carbonate was taken as reference material.

A 10 ppm solution of every metal was prepared and stored in clean Pyrex glass flasks. In the case of silver, a fresh standard solution was prepared before use.

Dry Ashing Procedure

In a silica crucible 5g oil was cleanly transferred. After covering with a proper lid the crucible was gently heated on a bunsen flame in a fuming cupboard. The oil started to burn slowly leaving a blackish residue at the bottom of the crucible. After complete combustion the heating was discontinued and warm residue was dissolved in 3 ml of concentrated nitric acid. The dissolution of residue may be facilitated by heating the crucible gently. Then the clean solution was transferred into a 100 ml flask. The crucible was rinsed twice with water and washings were also added to the flask. The volume of the flask was made upto the mark with water.

The solution was aspirated into a medium air-acetylene flame and absorbance due to various metal ions was measured under optimum conditions. The concentration of each metal ion was calculated from the calibration graph plotted for that metal ion.

Mixed Solvent System Procedure

2g of oil sample was transferred in a 100 ml flask already containing 15 ml of butan-2-one, 2 ml hydrochloric acid and 10 ml of isobutyl alcohol. The contents were shaken throughly to get a homogeneous solution. Then 10 ml of water was added to the flask and volume was made upto the mark with ethanol. The same solvent ration has been followed in preparing calibration standards. Absorbance of calibration standards as well as of sample solutions was measured against a compensatory blank prepared by the same volumes of solvent constituents.

Results and Discussion

Solvent Composition and Solubility of Oil Sample

Ratio of the solvent mixture had a pronounced effect on the solubility of oil samples. Relatively greater quantities of the oil sample could be easily dissolved in a solvent mixture with a greater percentage of organic solvents like butan-2-one or isobutanol. However the change in ethanol concentration showed a little effect on the solubility of oil, on the other had a solvent mixture containing lesser volumes of organic components and relatively greater quantities of water, acid and ethanol could dissolve smaller volumes of the samples after excessive shaking.

Homogenity of the solution has also been found a dependent factor of its composition. The solutions with relatively lesser aqueous content have been found more homogeneous for longer times as compared to the solutions containing greater quantities of water, acid and ethanol. Similarly a little shaking was required to dissolve relatively lesser volumes of aqueous content whereas the dissolution of greater quantities of water and acid, was tedious and time consuming.

Solvent composition and flame conditions

Originally a blue, lean and oxidising air-acetylene flame was used in this work. On aspirating the mixed solvent this flame turned slightly yellow and a little noisy. On increasing the organic content in the solvent mixture the flame became too much yellow, smoky and nearly opaque. The noise level of this opaque flame also became intolerable. Therefore in order to keep the flame conditions workable one has to keep a balance between the inorganic and organic contents of the solvent. However increase in ethanol concentration did not alter the flame conditions too much. Increase in the concentration of high molecular weight solvents like isobutanol affected the flame conditions more adversely as compare to low molecular weight solvents like methanol or acetone. The opacity of the flame is probably due to the incomplete combustion of carbon particles produced by the solvent components.

Effect of Time and Temperature

This has been noticed during this work that solubility of the sample in the mixed solvent and the homogeneity of the solution therefore were also affected by the time and temperature factors. If solution were kept at low temperature i.e. below 20°C for more than 12 hours they started to become turbid. This may be due to crystallisation of wax in the oil sample on standing at low temperature and finally an oily layer accumulated at the top. To redissolve this layer the solutions had to be heated in a water bath, with occasional shaking. However at 25°C and above the solutions were almost clear when placed for even more than 24 hours.

Precision

Precision of both the procedures, dry ashing and mixed solvent, was checked analysing eight samples of the same oil by each methods. The values obtained of standard deviation for both methods are shown in Table-1. As it can be seen from the Table that precision in the case of mixed solvent procedure is almost three times better than that of dry ashing procedure. The poor precision found in the dry ashing procedure can be attributed to the losses during combustion process and to the limited solubility of the residue in nitric acid.

Use of Acids

Concentrated nitric acid was used to dissolve the pure metals for standard solutions and the residue after combustion in dry ashing process. Hydrochloride acid 6M, was used as one of the constituents in mixed solvent to keep the metal ion in solution and to decrease the possibility of hydroxide formation especially for the ions with high charge density like iron(III). Through small quantities of these acids are not very effective on

Table-1: Trace Metals in Crude Oil Samples

Sample	Metals ppm											
	Na		K		Ca		Mg		Pb		Cd	
	Mix*	Ash**	Mix	Ash	Mix	Ash	Mix	Ash	Mix	Ash	Mix	Ash
Dabi No.1	13.70	10.5	8.65	6.34	12.90	10.45	4.12	4.00	0.35	0.18	0.35	0.20
Dabi No.2	11.54	8.2	5.12	5.82	15.45	12.85	2.83	2.85	0.30	0.26	0.57	0.40
T.Alam No.1	1.94	1.2	0.70	0.62	2.15	1.76	3.72	3.54	0.42	0.35	0.34	0.25
T.Alam No.2	1.32	0.75	0.74	0.55	2.22	1.84	3.55	2.92	0.05	0.05	0.25	0.12
T.Alam No.4	2.10	1.22	0.72	0.54	2.09	1.55	3.64	3.12	0.25	0.12	0.19	0.17
T.Alam No.5	2.15	1.58	0.68	0.42	2.05	1.67	3.72	3.52	0.32	0.14	0.08	0.05
T.Alam No.8	2.34	2.02	2.72	2.52	1.89	1.05	3.49	2.84	0.22	0.12	0.35	0.12
Mazari South 1	17.05	9.45	6.20	4.22	6.75	4.32	2.73	2.15	0.15	0.05	0.28	0.10
Mazari South 2	25.20	13.70	11.66	9.22	10.50	7.23	2.21	1.88	0.05	0.05	0.32	0.11
Laghari	0.25	8.20	6.74	4.32	4.25	4.20	1.94	1.66	0.05	0.05	0.27	0.09
Lockart	3.20	1.75	0.82	0.64	0.60	0.32	1.56	1.36	0.18	0.06	0.20	0.05
Khaskheli	5.10	3.75	0.74	0.54	0.32	0.20	4.30	3.56	0.20	0.06	0.16	0.05

*By mixed solvent system ** By Dry Ashing procedure.

Table-2: Trace Metals in Crude Oil Samples

Samples	Metals ppm											
	Fe		Cu		Ni		Cr		Mn		Zn	
	Mix*	Ash**	Mix	Ash	Mix	Ash	Mix	Ash	Mix	Ash	Mix	Ash
Dabi No.1	0.70	0.062	0.25	0.20	0.15	0.10	4.50	2.25	0.05	0.05	0.35	0.25
Dabi No.2	0.65	0.58	0.30	0.22	0.38	0.24	5.32	1.45	0.05	0.05	0.40	0.32
T.Alam No.1	0.29	0.15	2.25	1.82	0.15	0.10	9.15	6.25	0.08	0.05	0.75	0.35
T.Alam No.2	0.42	0.32	1.95	2.05	0.13	0.10	12.55	8.00	0.16	0.08	0.05	0.05
T.Alam No.4	0.47	0.27	2.62	2.14	0.19	0.05	5.72	4.52	0.15	0.07	0.07	0.05
T.Alam No.5	0.32	0.22	2..45	2.32	0.25	0.15	8.54	6.35	0.13	0.07	0.05	0.05
T.Alam No.8	0.35	0.34	2.36	2.40	0.14	0.05	15.00	12.05	0.15	0.08	0.15	0.05
Mazari South 1	0.29	0.15	1.90	1.56	0.54	0.32	8.50	6.35	0.08	0.05	1.92	1.40
Mazari South 2	0.38	0.32	1.65	1.50	0.64	0.42	7.52	5.12	0.08	0.05	1.54	1.02
Laghari	0.52	0.42	0.46	0.30	0.27	0.15	5.95	5.72	0.15	0.05	0.32	0.08
Lockart	0.33	0.29	0.58	0.48	0.35	0.21	5.90	3.67	0.10	0.05	0.25	0.07
Khaskheli	0.47	0.45	1.22	1.20	0.30	0.27	5.75	4.82	0.16	0.06	0.16	0.05

*By Mixed solvent system ** By Dry ashing procedure.

the absorption of metal ions concerned but to avoid the possible interferences equal volumes of acids have been used in the blank, standards and samples.

Samples

Twelve samples from various oil fields of Pakistan were collected and analysed for sodium, potassium, calcium, magnesium, iron, copper nickel, manganese, cadmium, chromium, zinc and lead. The results obtained by both methods are presented in Table-1. Attempts were also made to determine the elements like silicon, tin and vanadium but the only available flame, air-acetylene was not suitable enough to get reliable results for these elements.

As shown by Tables-1 and 2, there is a significant difference in most of the results obtained by mixed solvent procedure and dry ashing procedure. Results obtained by ashing procedure are generally low than those obtained by solvents method. This difference in results is mainly due to the losses occured during combustion process. The difference in results is quite evident in the cases of sodium and potassium. Exceptionally high values of sodium and potassium in certain cases may be incidental due to the contact of crude oil with salt water.

Conclusions

Mixed solvent system used in this work proved itself a quick, precise and relatively easy method for determining metal constituents in crude oil samples. Composition of solvent mixture can be easily adjusted according to solubility of the sample and the flame conditions. Another advantage which this method offere is that relatively cheeper and easily available inorganic standards can be used as reference materials.

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