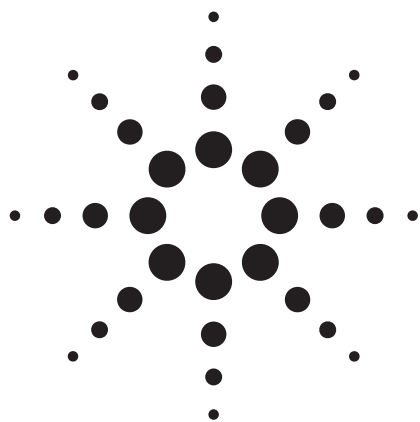




Analysis of Used or Waste Oils by Method 3040 of SW-846 by ICP-OES

Application Note

Inductively Coupled Plasma-Optical Emission Spectrometers

Author

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Introduction

The analysis of lubricating oils has been well documented for many years. With passing of the Resource Conservation and Recovery Act (RCRA), the United States Environmental Protection Agency (USEPA), 40 CFR, Part 279, requires that used or waste oils (primarily used engine crankcase oils) be analyzed for metallic content prior to disposal. The disposal of the used oil can vary. Methods of disposal are:

1. Hazardous waste mixing
2. Used oil storage
3. On-site burning (Industrial or in Space Heaters)
4. Off-site shipments
5. Dust suppression
6. Processing or reprocessing

The industrial burning of used oils is described in Subpart G, paragraph 260.10. The burning for industrial purposes include:

1. Industrial furnaces
2. Boilers
 - a. Industrial boilers
 - b. Utility boilers
 - c. Oil fired space heaters (ppg 279.23)
3. Hazardous waste incinerators (Subpart O of Parts 264 or 265)



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The four metals of interest are arsenic (As), cadmium (Cd), chromium (Cr) and lead (Pb). The maximum acceptable levels of each metal are shown in Table 1.

Table 1. Maximum Allowable RCRA Metal Content in Waste Oils

Arsenic	5.0 ppm
Cadmium	2.0 ppm
Chromium	10.0 ppm
Lead	100.0 ppm

A simple technique for sample preparation of lubricating oil is dilution with a suitable solvent, such as kerosene and xylene, followed by analysis. This method is commonly known as dilute and shoot analysis. This sample preparation technique can easily be applied to the waste oils for the analyses required by RCRA.

Sample Preparation

The sample preparation specified by RCRA is Method 3040 of the SW-846 Methods. Method 3040 covers the analysis of oils, waxes and greases by atomic absorption spectroscopy (AAS) or inductively coupled plasma atomic emission spectroscopy (ICP-OES). The method suggests the use of an appropriate solvent such as xylene or methyl isobutyl ketone.

The sample submitted was analyzed for the four metals in Table 1. The submitter requested the samples be diluted with kerosene. The samples were diluted using the weight/weight technique. Additionally, the sample was split; the split sample was run in duplicate and each split was spiked.

Using this technique, five grams of blank (base oil), standards, and samples were weighed into a 50 mL conical, disposable centrifuge tube. An additional gram of base oil was added to each solution, except the spiked samples, to compensate for the one gram of oil standard used to determine a spike recovery. Finally, all the solutions were brought to a 25 gram final weight with reagent grade, odorless kerosene.

The standards for Cd, Cr and Pb were prepared using Conostan S-21 standards. The standard concentrations were 10 ppm, 50 ppm and 100 ppm for Pb and Cr. The Cd standard concentrations were 5 ppm, 10 ppm, 50 ppm and 100 ppm. Because the arsenic standard is only available in 100 ppm, dilution with base oil was necessary to prepare the desired concentration range. The arsenic standards of 10 ppm, 50 ppm and 100 ppm were prepared by weighing 0.5, 2.5 and 5.0 grams of the standard to the centrifuge tube. Base Oil 75 was added to each standard to bring the weight to 6 grams and then kerosene was added to bring the final weight to 25 grams.

The results for arsenic and cadmium were higher than expected when the arsenic standard was mixed with the S-21 standard that contained the cadmium. This was not a consequence of the well-known spectral interference of arsenic and cadmium at 228 nm, because this line was not used for either element. The As and Cd lines used (Table 2) are not subject to spectral overlap.

The arsenic and S-21 standards are in different base oils, and different organic salts are used. The manufacturer states that S-21 is incompatible with the arsenic, selenium and phosphorus standards and they should not be mixed. In an attempt to lessen the number of solutions prepared, and shorten the preparation time, the manufacturer's recommendations were ignored and the standards were mixed. This led to unsatisfactory recoveries. The standards and samples for arsenic had to be prepared separately from those used to determine cadmium, chromium and lead.

The 50 ppm standard was used as the QC standard at the beginning and the end of each analysis.

Each sample was spiked to determine the spike recovery of the analysis. One gram of the 100 ppm S-21 and arsenic standard was added to the respective samples. The resulting spike concentration in all samples was 20 ppm for all the metals.

Instrumentation

The Liberty 220 Inductively Coupled Plasma-Atomic Emission Spectrometer was used in this analysis. The Liberty was configured with the Sturman-Masters Spray Chamber and the standard one-piece torch. Because the sample was used oil, the glass concentric nebulizer was replaced with a V-groove nebulizer to minimize potential problems with particulates known to exist in used lubricating oil samples. Additionally, the Argon Saturator Accessory was disconnected to prevent the formation of emulsions in the nebulizer and spray chamber. Formation of emulsions results in blockages or plugging of these components.

The instrument parameters for the Liberty 220 are shown in Tables 2 and 3.

Table 2. Metal Specific Liberty 220 Instrument Parameters

	As	Cr	Pb	Cd
Wavelength (nm)	188.979	267.716	220.553	226.502
View height (nm)	3	5	3	3
Windows search (nm)	0.015	0.040	0.027	0.027
Scan (nm)	0.025	0.060	0.040	0.040
Integration (s)	3.00	3.00	3.00	3.00
Replicates	3	3	3	3
Filter position	1	6	1	1
Order	3	2	3	3
PMT (V)	700	700	700	700
Power (kW)	1.25	1.25	1.25	1.25
Plasma flow (L/min)	13.5	13.5	13.5	13.5
Auxillary flow (L/min)	1.50	1.50	1.50	1.50
Pump speed	15	15	15	15
Background mode	Dynamic	Dynamic	Dynamic	Dynamic
Mode units	ppm	ppm	ppm	ppm
Max curve order	1	1	1	1
Weighted fit	Yes	Yes	Yes	Yes
C.C. limit	0.995	0.995	0.995	0.995

Table 3. Liberty 220 Common Parameters

Nebulizer pressure	150 kPa
Stabilization time	15 s
Sample delay time	15 s
Rinse time	60 s
Snout purge	OFF

The viewing height for each line in the program was optimized by intensity. The order and search window were optimized to minimize or eliminate any problems with interferences. The primary interferences were from band structures from the organic solvents and components present. No spectral interferences were found with these samples.

The samples were introduced manually into the instrument. The rinse time was timed using a stop watch. It was necessary to rinse between standards and samples to ensure there was no carry over and that any particulates were washed out.

Results

The results for each sample split, Sample 1 and 2, and the duplicate analysis for each are in Table 4. The relative percent difference (%RPD) is included in the table.

Table 4. Analytical Result of Samples and Duplicates (Expressed in ppm)

Element	Split	Sample	Duplicate	%RPD
As	#1	-2.87	-3.74	-26.4
	#2	-5.68	-7.08	-22.0
Cr	#1	2.60	2.48	4.6
	#2	2.54	2.49	1.7
Pb	#1	47.2	46.1	2.4
	#2	45.9	45.7	0.5
Cd	#1	2.04	1.93	5.4
	#2	1.95	1.91	2.5

The spike recovery results are in Table 5. Each split sample was spiked as described in the sample preparation section of the At Work.

Table 5. Spike Recovery Results

Element	Split ppm	Actual ppm	Found ppm	%R
As	#1	20	20.2	101.0
	#2	20	17.8	89.1
Cr	#1	20	18.4	91.9
	#2	20	18.6	93.0
Pb	#1	20	21.8	109.0
	#2	20	23.1	115.7
Cd	#1	20	22.2	111.2
	#2	20	22.4	111.9

Finally, the calibration verification results are expressed in Table 6. The 50 ppm standard was used as the calibration check solution. The calibration was checked prior (ICV) to analysis of the samples and at the end of the analysis (CCV).

Table 6. Calibration Verification Results, % Recovery

Element		Solution found (ppm)	%R
As	ICV	47.5	95.1
	CCV	48.5	96.9
Cr	ICV	46.7	93.4
	CCV	46.9	93.7
Pb	ICV	48.0	96.1
	CCV	49.5	99.0
Cd	ICV	49.1	98.3
	CCV	49.7	99.3

Conclusion

The analysis of used oils by dilution with an appropriate solvent, as described in Method 3040 of SW-846, is a simple and sufficiently accurate method.

The analysis is reproducible as shown by the duplicate results in Table 4. Except for the As, the RPD of the Duplicate Test is 5 %RPD or below. There is no arsenic in the samples and as a result the %RPD is rather large, as would be expected statistically. The reproducibility of the analysis is excellent.

The spike recoveries for the analysis are very good. The USEPA normally requires a spike recovery of 85% to 115 % recovery. Referring to Table 5, all the recoveries are well within the $\pm 15\%$ except for the second Pb spike. The recoveries may improve with a longer rinse between samples to reduce the build up of particulates from the sample matrix.

Finally, the ICP is a stable, accurate instrument for the analysis of the used oils. The calibration verification results in Table 6 show all the verification solutions well within the $\pm 10\%$ recovery required by the EPA.

The analysis of the used oils is easily performed with simple dilution with an appropriate solvent, followed by analysis by ICP-OES. The analysis is fast, accurate and reproducible. The V-Groove nebulizer, to minimize problems with particulates in the sample, is the only additional accessory required for the analysis.

References

1. Standards for the Management of Used Oils, CFR, Title 400, Part 279, Federal Register 40:279 (July **1994**) pp856-882.
2. Dissolution Procedure for Oils, Greases and Waxes, Method 3040, SW-846, Volume IA, Test Methods for Evaluating Solid Waste, United States Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC 20460 Third Edition, November **1986**.

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