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Preparation of Petrochemical Samples for Atomic Absorption Spectrometer

Atomic Absorption Spectrometry (AAS) plays a pivotal role in the elemental analysis of petroleum products, encompassing three significant areas: crude oil assessment, fuels and lubricants analysis, and wear metal identification. In this context, Flame AAS is typically employed for determining metals present in higher concentrations, while graphite furnace techniques are utilized for the analysis of trace metals. This distinction ensures accurate and sensitive measurements for various components in petroleum products.

Sample Preparation Procedure

In the determination of metals in petroleum products, three primary sample preparation methods are commonly utilized:

1. **Dilution:** The petrochemical sample is diluted with an organic solvent, such as methyl isobutyl ketone (MIBK) or a mixed solvent system like toluene and glacial acetic acid.
2. **Ashing and Dissolution:** The sample is subjected to ashing, followed by dissolution with a suitable acid.
3. **Acid Digestion:** Acid digestion is employed to prepare the sample for metal analysis.

These sample preparation methods ensure the accurate measurement of metals in petroleum products, catering to the diverse requirements of analytical procedures.

Dilution

While some petrochemical samples can be directly nebulized into a flame or injected into a graphite furnace for analysis, there are situations when dilution is necessary. This occurs when the sample is excessively volatile, highly viscous, or contains an exceptionally high concentration of the element of interest.

Dissolving oil and fuel samples in organic solvents is a straightforward and rapid process. The extent of dilution and the choice of solvent are contingent upon various factors, including the sample's characteristics, the anticipated level of the element being analyzed, and any background signals observed during atomization. The volatility of the chosen solvent significantly influences the selection of drying conditions and the potential use of an autosampler.

In cases where evaporation poses a challenge, it's advisable to seal the sample container and dispense the sample manually. Alternatively, a less volatile solvent can be utilized. Mixed solvent and emulsion systems offer the flexibility of using inorganic salts for preparing standards and calibration curves.

Table 1 provides a list of commonly used organic solvents in oil and fuel analysis, along with their boiling points. These boiling points serve as a reference for establishing drying conditions when employing Graphite Furnace Atomic Absorption Spectrometry (GFAAS). With conventional furnace techniques (not fast drying), most solvents can be effectively dried at temperatures below their boiling points. In most analyses, a drying step at a temperature setting ranging from 80 to 90% of the boiling point for 30 to 60 seconds is typically sufficient when working with a 20 to 40 μL sample. It is advisable to assess the dispensing characteristics of the solvent before analysis to determine the maximum injection volume, which can vary based on the solvent's surface tension. Generally, injection volumes in the range of 20 to 40 μL are employed.

Solvent	Boiling point (°C)	Specific gravity
Kerosene	175 - 325	0.78
Tetralin	207	0.97
Shellsol T	186 - 214	0.75
DIBK	166	0.81
Cyclohexanol	161	0.96
3-heptanone	148	0.82
m-xylene	139	0.80
Iso-amylalcohol	132	0.81
MIBK	118	0.79
Toluene	112	0.86
2-methy, propan-1-ol	108	0.78
Isopropanol	83	0.78
Carbon tetrachloride*	77	1.59
Tetrahydrofuran*	65	0.88
Chloroform*	62	1.47

* Not suitable form flame AAS

Table 1. Solvents commonly used as diluents in AAS

Ashing of the Oil Sample

The procedure for ashing oil is based on the method developed by Milner, Glass, Kirchner, and Yurick (Anal. Chem., 24, 1728 (1952)). The following method is employed for the analysis of iron:

A 2-gram oil sample is combined with 2 grams of concentrated sulfuric acid. This mixture is then heated on a hot plate until it is completely dry. This process is carried out in a vycor crucible. The vycor crucible is subsequently transferred to a muffle furnace and subjected to ashing at 550°C. This ashing continues until all traces of carbon are eliminated. The absence of a charcoal color, which typically takes about 30 minutes, indicates the removal of carbon. After cooling, the ashed sample is treated with 6 mL of concentrated hydrochloric acid and then filtered through a Whatman filter paper. The resulting solution is brought up to a final volume of 25 mL using pure water.

It's important to note that this ashing method provides a measure of the total metal content, representing the sum of both particulate and soluble metals. However, it should be recognized that volatile metals, such as lead and selenium, are lost during the ashing process.

Acid Digestion

Acid digestion of oil samples is a method that allows for the preservation of volatile elements which may otherwise be lost during ashing or obscured by background interference. In recent years, microwave oven-assisted acid digestion has seen a surge in popularity. This advanced technique significantly expedites and simplifies the acid digestion process. You can find references on the digestion of oil samples with acids in the available literature.