



## **MEASUREMENT OF ALKALI METALS IN GAS TURBINE LIQUID FUELS**

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This position paper does not purport to cover all details or variations in the issue discussed nor to provide for every possible contingency to be met in connection with the chemical analysis of liquid fuel oils. If further information is required, or should particular problems arise which are not covered sufficiently covered, the matter should be referred to GE Power Systems.

## MEASUREMENT OF ALKALI METALS IN GAS TURBINE LIQUID FUELS

### INTRODUCTION

An important issue facing operators of liquid fuel fired gas turbines is contamination of the fuels with salts of alkali metals. Burning contaminated fuel can result in the formation of sodium and potassium sulfates during the combustion process and the deposition of these salts in the hot gas path, where they are highly corrosive to the metals from which the combustion liners, transition pieces and airfoils are made. To prevent this corrosion the specification GEI 41047 limits the combined sodium and potassium (Na+K) content of liquid fuel to 1 ppm.

This limit assumes that all the alkali entering the turbine is in the fuel. If other mass flows entering the turbine, such as air, steam or water also contain alkali, then this must be accounted for by reducing the allowable alkali in the fuel.

The operating limit is 20 ppb Na+K in the combustion gas of liquid fuel burning Model B, E, EA, F and FA turbines.

The calculation of allowable alkali entering the gas turbine is discussed in detail in GEK 107230 "Specification for Alkali Metal Contamination in Fuels".

### ANALYSIS OF LIQUID FUELS.

Alkali metals are present in liquid fuels dissolved in the small drops of water which are dispersed in the fuel. Typically the water content of a crude oil will be 0.1% or less as it enters the turbine fuel skid and this water will contain all the alkali metal contamination. Depending on the fuel type and its history, the distribution of the water, and hence the distribution of the alkali metals, may be very non-uniform in both the bulk fuel and the samples taken from it. Because of this, the analysis of crude fuel oil for alkali metal content presents several challenges:

1. Obtaining a representative sample from the bulk oil. Uncertainty in sampling can be offset by taking multiple samples at each point where fuel is sampled and comparing analysis results.
2. Introducing a representative sample to the analyzer. This requires that the samples be well mixed and that the instrument takes in a representative flow from the mixture of oil and water. It has been observed that instruments which use fine tube sample aspiration systems will not uniformly aspirate a mixture of oil and water.
3. Choosing a method/instrument, which has suitable accuracy and detection limits for sodium and potassium in the concentration range 0.1-2.0 ppm.

Before discussing the different methods available for the analysis of alkali in fuel it is necessary to define some chemical terms.

### ANALYTICAL CHEMISTRY TERMS

**A signal** is the output of an instrument that is responding to the alkali specie of interest. The signal may be divided into two parts, one caused by the specie of interest in the sample (Na, K), and the other caused by other components of the

sample matrix and the instrumentation used in the measurement. This latter part of the signal is known as **noise**.

The ability of an instrument system to discriminate between signal from the alkali and noise is usually expressed as a signal-to-noise ratio (S/N), where

$$\frac{S}{N} = \frac{\text{average signal amplitude}}{\text{average noise amplitude}}$$

in the case of dc signals. An increase in the S/N ratio usually indicates a reduction in noise and thus a more desirable measurement.

Once the physical or chemical quantity being measured is converted to an electrical signal, the S/N ratio cannot be increased by simple amplification alone, since each increase in the magnitude of the signal is accompanied by a corresponding increase in the value of the noise.

The **standard deviation or repeatability** of a measurement is the difference between successive tests obtained by the same operator testing the same fuel sample in the same instrument.

**Detection limit** is the smallest alkali concentration that can be measured by a method and is that concentration which produces a signal that is at least twice the standard deviation of the signal obtained in the blank measurement.

**Sensitivity** is the ratio of the change in the instrument response ( $I_o$  output signal) to a corresponding change in the stimulus ( $C_o$  concentration of the alkali):

$$S = \frac{dI_o}{dC}$$

Sensitivity can vary over the range of measured concentrations, whereas the detection limit is measured in the region where the signal disappears into the noise.

#### **REQUIREMENTS OF THE TEST METHOD.**

ASTM D-3605 is the Standard Test Method for Trace Metals in Gas Turbine Fuels by Atomic Absorption and Flame Emission Spectroscopy. In section 1.1 of the Scope of the method it is stated that the method is "intended for the determination of oil-soluble metals and not for waterborne contaminants in oil-water mixtures."

The alkali metals, sodium and potassium, are not present as oil soluble compounds but are dissolved in the water, which is mixed in the oil. This is clear from the methods which are typically used to remove alkali metals from crude fuel oil. Namely, water washing, centrifuging and electro-desalting. The vanadium on the other hand, which can be measured accurately using method D 3605, is present as an oil soluble compound and cannot be removed by washing, centrifuging or desalting.

The accurate direct measurement of alkali in crude fuel oil depends on sample preparation, which distributes the water uniformly in the oil and a sample injection

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method that takes a representative sample into an analyzer, which has a suitable detection limit.

Specification GEI 41047 requires measurement of alkali in the 0.1 to 1.0 ppm concentration range. In order to do this, the limit of detection of the instrument should be 0.1 ppm or less, which requires a standard deviation or repeatability of 0.05 ppm or less.

### **TEST METHODS.**

#### **ATOMIC ABSORPTION SPECTROSCOPY (AAS).**

AA Spectroscopy can produce accurate and reliable results for alkali metals in crude fuel oil. The method requires careful preparation, handling and analysis of samples by expert staff. The repeatability for sodium (and by extension, potassium) is 0.07 ppm and the reproducibility is 0.21 ppm (the 2-sigma limit of detection is two times the repeatability or 0.14 ppm). This detection limit and repeatability is adequate to measure levels of sodium and potassium in the range 0.1 to 1 ppm.

Capable analytical laboratories can perform accurate fuel analysis using ASTM D3605 by atomic absorption spectroscopy. The method requires a controlled laboratory environment with skilled chemists and is not appropriate for rapid analysis of multiple samples in a power plant.

#### **ATOMIC EMISSION SPECTROSCOPY (AES) ICP SPECTROSCOPY.**

Many commercial laboratories offer alkali metals analysis by ICP spectroscopy. For most elements, ICP spectroscopy is the analysis method of choice in today's modern laboratory because of the very low detection limits achievable, as well as the speed and accuracy of the analysis, However, ICP spectroscopy is not well suited for alkali metal analysis for a variety of reasons.

1. The limits of detection are too high. A typical limit of detection for sodium in water or kerosene by ICP spectroscopy is 0.3 ppm. This is not good enough for accurate measurements at or below 1 ppm.
2. If the fuel sample must be diluted, which is often the case for proper nebulization, the limit of detection increases by the dilution ratio. This will make the effective limit of detection greater than 1 ppm. This makes the method entirely inappropriate for alkali metal analysis in the 0.1-1.0 ppm range.
3. The stability of standard solutions following dilution is quite limited and can introduce further errors to the methods.
4. The calibration practices of commercial laboratories may introduce inaccuracies. A sample containing 0.5 ppm of Na may be measured on an ICP spectrometer which has been calibrated with a 100 ppm standard solution.
5. A very serious problem is the inability of the nebulizer to introduce a representative sample into the plasma when the solution which is being tested is heterogeneous, as is the case with a sample which contains water suspended in crude oil.

For all these reasons it is recommended that ICP Spectroscopy not be used for the measurement of alkali metals in fuel oils.

**ATOMIC EMISSION SPECTROSCOPY (AES)  
FLAME OR ARC/SPARK SPECTROSCOPY**

A much superior alternative to ASTM D3605, for on-site testing for alkali in fuels, is the use of flame emission spectroscopy using the rotating disc electrode technique per ASTM D6728.

In flame emission spectroscopy, the sample is introduced to a combustion flame or an electric arc or spark where the alkali metal salts are converted to excited state atoms in the vapor phase and emit light as they return to their ground state. The light emitted is proportional to the alkali in the sample.

FES offers the lowest detection limits for alkali metals. Because of this, as well as the reliability, simplicity and ruggedness of the FES spectrometers, it is the method of choice for alkali metal analyses in industry. FES analyzers do not require operators with the higher level skills and training needed with the AA and ICP machines.

A very convenient type of FES analyzer is that employing the rotating disc electrode (RDE). The RDE method does not require sample dilution and limits of detection (2 sigma) for sodium and potassium of 0.05 ppm are typical in modern instruments. A major advantage of the RDE spectrometer is the way that the sample is introduced to the test, which allows representative sampling of an oil-water mixture.

The ASTM D2 committee on Elemental Analysis developed an ASTM (D6728) method for trace analysis of metals in gas turbine fuels by flame emission spectroscopy using an RDE spectrometer.

**RECOMMENDATION.**

GEPS recommends that the analysis of alkali metals in crude oil is performed by Atomic Absorption Spectroscopy or by Flame Emission Spectroscopy, using a rotating disc electrode spectrometer. The latter method is strongly recommended for use in the Power Plant laboratory.