

The Measurement of Silicon, Tin, and Titanium in Jet-Engine Oil

Application Note

Atomic Absorption

Author

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Introduction

The analysis of used engine oils by spectrometric techniques for the early detection of machine component failure has been an important area of investigation since first applied by railroad companies in the 1940s [1].

The long term monitoring of wear metal levels in lubricating oils has been undertaken by the armed services, major road transport companies, tractor manufacturers, airlines and railways.

A wear metal profile is often prepared for each engine. Typically an early wear-in period of high metals concentration is observed, followed by a plateau of low metals concentration [2]. Impending component failure will be indicated by a rapid increase in wear metal concentration, or the sudden appearance of a metal. The metal type and concentration may also indicate to the analyst and engineers which part of an engine is failing. A change in the concentration of sodium for example, may indicate an antifreeze leakage, the increased presence of lead may indicate the wear of bearings in a diesel engine [3].

Many different analytical techniques have been applied to wear metal investigations. The most widely used technique for wear-metal analysis in the last decade has been flame atomic absorption spectroscopy (FAAS) [4]. In more recent times, graphite furnace AAS and atomic emission spectroscopy (AES) methods have been increasingly employed.

Despite this interest and continued development, cases have been documented where a Spectrometric Oil Analysis Program (SOAP) has failed to predict aircraft oil-wetted component failure [3]. This has been attributed to limitations in the particle size detection capabilities of major SOAP techniques such as rotating disk electrode AES and flame AAS.



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Typically wear-metal particles less than 1 micron in dimension can be readily determined by spectrometric techniques, but particles greater than 5 microns (indicative of more severe wear) may go undetected. This problem is usually caused by the inability of the sample transport system to move such particles or to the failure of an atomization process to break up the particles so that their components can be atomized. In addressing this problem C. S. Saba and co-workers have developed Particle Size Independent Methods (PSIM) for wear-metals by the reaction of the used oil sample with a mixture of hydrofluoric, hydrochloric and nitric acids [1,5–9].

In a recent publication, however, Saba et al. [1] noted in a comparative study of spectrometric analysis techniques, that only a graphite furnace atomization AAS method was capable of analyzing iron particles from the submicron to 20–30 micron (unfiltered) size, as was the PSIM developed by these workers. Flame AAS, inductively coupled plasma AES, rotating disk AES and DC argon plasma spectrometry all showed serious particle size detection limitations.

In the study described here, the capabilities of the Agilent GTA-96 graphite furnace AAS system were examined for the determination of silicon, tin and titanium in jet-engine oils. These elements were selected because:

- They are reported relatively infrequently in the literature [4].
- They exhibit relatively poor sensitivity when determined by conventional flame AAS techniques [10].
- They are of vital interest in jet-engine oil analysis programs.

Table 1 [2,3,13] indicates the possible sources of these elements in engine oils and lists the expected flame AAS working ranges for these elements. The use of graphite furnace atomization with autosampling in this work, allows greater sensitivity with smaller sample consumption.

Table 1. Element Sources in HJet-Engine Oils and Flame AAS Working Ranges

Element	Possible source in engine oil	Flame AAS working range (aqueous) µg/mL
Silicon	Dirt and sand intrusion (may indicate need for air cleaner service), silicon lubricant leaks silicon tubing failure, silicon seals failure	3–400
Tin	Journal bearings, bearing cages and retainers, coatings on connecting rods, and iron pistons	1–200
Titanium	Aircraft casings	1–300

Instrument Parameters

Silicon (flame)

Spectrometer	Agilent SpectrAA-40
Instrument mode	Absorbance
Calibration mode	Concentration
Measurement mode	Integration (3 seconds)
Flame	Nitrous oxide-acetylene
Acetylene	6.51 liters/minute
Nitrous oxide	11.8 liters/minute
Wavelength	251.6 nm
Slit width	0.2 nm
Lamp	Agilent; silicon HC
Lamp current	10 mA

Silicon (furnace)

Spectrometer	Agilent SpectrAA-40
Autosampler	Agilent
Instrument mode	Absorbance
Calibration mode	Standard additions
Measurement mode	Peak height
Furnace	Agilent GTA-96
Gas	Normal: nitrogen
Wavelength	251.6 nm
Slitwidth	0.2 nm
Lamp	Agilent; silicon HC
Lamp current	10 mA

Tin (furnace)

Spectrometer	Agilent SpectrAA-40
Autosampler	Agilent
Instrument mode	Absorbance
Calibration mode	Standard additions
Measurement mode	Peak height
Furnace	Agilent GTA-96
Gas	Alt: argon
Wavelength	235.5 nm
Slit width	0.5 nm
Lamp	Agilent; tin HC
Lamp current	7 mA

Titanium (furnace)

Spectrometer	Agilent SpectrAA-40
Autosampler	Agilent
Instrument mode	Absorbance
Calibration mode	Standard additions
Measurement mode	Peak height
Furnace	Agilent GTA-96
Gas	Alt: argon
Wavelength	364.3 nm
Slit width	0.5 nm
Lamp	Agilent; titanium HC
Lamp current	20 mA

Standard Preparation

Multielement organometallic standards in Mobil Jet-Oil II were supplied by an Australian organization operating a SOAP for aircraft maintenance. The concentrations ranged from 5 to 200 µg/mL, and contained the elements: Ag, Fe, Mg, Cu, Al, Si, Cr, Sn, Ni and Ti. These concentrated standards were less than five months old.

For the determination of silicon by flame AAS, standards were diluted four-fold (1 part standard plus 3 parts solvent) with MIBK (methyl isobutyl ketone, BDH Analar grade) to achieve the required concentrations. Standard dilutions were identical to ensure matrix matching.

For the determination of silicon, tin and titanium by GTA-AAS, the standard additions method of calibration was used to ensure matrix uniformity. Standards were diluted as necessary with MIBK.

Sample Preparation

A sample of used oil from a jet-aircraft engine, was diluted five fold in MIBK (1 part sample plus 4 parts solvent) for the determination of tin and titanium.

Sample Handling Notes

The handling of both thick oils and low viscosity volatile organic solvents for wear-metals in oils analysis requires different sampling protocols.

Some points to consider are:

- Oil samples and standards will settle with time. Agitating the sample oil in an ultrasonic bath for several minutes prior to or during sampling provides a convenient method of overcoming this problem.
- Two techniques are used for the reproducible measurement of sample size – weight and volume. Sample weighings offer convenience in terms of reproducibility. Sample volume measurements require a strict protocol regarding pipette filling and draining procedures. A typical drain time could be as long as one or two minutes for viscous fluids. Care must be taken to ensure no fluid is carried on the outside of the pipette. Dilutions in this work were carried out by volume measurement.

- Samples and standards should be stored at low temperatures to guard against evaporation of volatile solvents. Fresh dilutions of concentrated standards should be made before the start of the analytical program of each day. Low concentration standards (less than 1 µg/mL) may deteriorate over a period of days.
- Contamination and toxicity also present specific problems in oil analysis. Volatile solvents should be handled in a fume cupboard.
- The autosampler should be protected with its dust cover and in many solvent handling situations the operator would be advised to wear gloves.
- Safety practices for the handling of organic solvents, particularly for flame AAS, must be strictly followed. A good summary of these practices can be found in reference [11].
- Reproducible sampling techniques are a major step towards achieving reproducible results. When sampling from the aircraft it is recommended [2] that the sample be taken when the engine is at normal operating temperature. A sampling tube is inserted into the dipstick port to a specified depth and the sample withdrawn by syringe (5–20 mL).

To achieve optimum results care must be taken with the graphite furnace sampler alignment when using organic solvents. The low viscosity of the organic solvents requires the positioning of the dispensing tip much closer to the furnace wall than would be the case for aqueous samples.

This ensures that the solvent does not creep back up the outside of the sampler tip, which would cause errors in the volume dispensed. A further problem of creep can occur if the dispensed sample expands as the tube is heated and a small amount rises out through the tube hole, after creeping along the tube walls. This increases tube wear and adversely affects precision. The problem can be overcome by careful sample alignment. The tip should be kept low and central in the tube and small sample volumes should be used (10–20 microlitres). The graphite tube was of the partitioned type which is especially suitable for organic solvents.

The autosampler rinse solution was made up of approximately 0.001% Triton X detergent and 0.002% nitric acid. Use of this rinse solution ensures thorough cleaning of the sampler tip to give proper dispensing without contamination.

Results and Method Development

Silicon In Jet-Engine Oil By Flame MS

For the determination of silicon by flame AAS, the uptake rate for the diluted samples and standards was set at 2.7 mL/minute. Samples and standards were all prepared in MIBK.

Selection of the uptake rate was a compromise between minimum flame flare-up, absorbance noise, avoiding flame lift-off in the absence of solvent, minimizing sample consumption and achieving maximum sensitivity. Background correction was selected, but it is not strictly necessary as the background from the flame was virtually eliminated by the optimization of conditions.

Carbon build-up on the burner slot may occur especially when using fuel-rich nitrous-oxide acetylene flames. This was not found to be a problem with the silicon determination, but several precautions were taken to minimize the possibility of build-up. The burner was cleaned thoroughly before analysis in a detergent concentrate in an ultra-sonic bath. The burner was then rinsed with tap-water and distilled water. The burner was dried with a blast of air. After installing the burner and igniting the flame, the burner was allowed to warm up completely on a lean flame prior to setting the gas flows required for the analysis. When developing a suitable method, the preferred conditions for minimum carbon build-up are: high total gas flows and the leanest flame possible. In the subsequent silicon determination no visible carbon build-up occurred in the time required to produce a calibration graph and sample results.

Results obtained are shown in Table 2. Acceptable levels of precision for silicon determination could be predicted from this data for levels above 10 µg/mb. The calibration graph in Figure 1 shows a high degree of linearity even at low levels. Error bars are shown in this graph which reflect the precision of the replicate measurements.

From these results a characteristic concentration can be calculated for silicon analysis in jet-engine oil. The characteristic

Table 2. Silicon by Flame AAS – Analytical Results

Sample	Program 5	Si Jet oil	Mean ABS
	Conc (ppm)	%RSD	
Blank	0.00		0.002
Standard 1	2.50	7.8	0.009
Standard 2	5.00	6.3	0.016
Standard 3	25.00	1.2	0.074
Standard 4	50.00	0.3	0.146

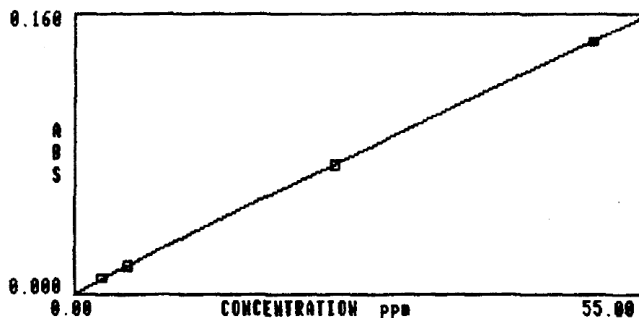


Figure 1. Silicon by flame AAS – calibration graph.

concentration (CC) is that concentration which gives an absorbance of 0.0044. The value obtained from this analysis (1.5 µg/mL) is the same as the expected literature value [12] for aqueous samples.

Silicon In Jet-Engine Oil By Furnace AAS

The determination of low levels of silicon in jet-engine oil is greatly facilitated by the use of graphite furnace AAS. Although individual measurement times are longer than those for flame AAS, the following advantages enhance its applicability:

- After initial program development and system set-up, virtually unattended operation is possible
- Improved sensitivity
- Reduced risk from the use of flammable solvents
- Greatly reduced sample consumption

A deuterium background corrector was used. The furnace program developed is presented in Table 3. The program consists of a two-stage dry phase, ashing at 1000 °C and atomization at 2700 °C. The sheath gas used was nitrogen, it would be expected that argon would give greater sensitivity. The other instrumental conditions were the same as used for the flame determination.

Table 3. Silicon by Graphite Furnace AAS – Furnace Parameters

Step no.	Temperature (C)	Time (sec)	Furnace parameters		
			Gas flow (L/min)	Gas type	Read command
1	40	0.1	3.0	Normal	No
2	80	10.0	3.0	Normal	No
3	150	10.0	3.0	Normal	No
4	150	60.0	3.0	Normal	No
5	1000	10.0	3.0	Normal	No
6	1000	10.0	3.0	Normal	No
7	1000	3.0	0.0	Normal	No
8	2700	0.9	0.0	Normal	Yes
9	2700	2.0	0.0	Normal	Yes
10	2700	3.0	3.0	Normal	No

The automatic sampler parameters are presented in Table 4. The programmable sample dispenser used with the GTA-96 automatically mixed the standard additions for deposition in the furnace. The total volume dispensed was 20 microlitres. The standard solution was 25 ng/mL of silicon.

Table 4. Silicon by Graphite Furnace AAS – Sampler Parameters

	Sampler parameters volumes (µL)			
	Standard	Sample	Blank	Modifier
Blank	–	–	20	
Addition 1	5	5	10	
Addition 2	10	5	5	
Addition 0	–	5	15	

Figure 2 is a signal graphics trace for a typical standard additions signal. It is evident from this trace that background levels are negligible, while the atomic signal is sharp and symmetrical. The temperature profile is also shown on these signals graphics.

Table 5 shows the results obtained from this analysis. The precision of the measurement (%RSD) is good. The calibration graph is presented in Figure 3. The characteristic concentration calculated from this data is 7 pg. This compares favorably with the literature value of 25 pg [13]. Based on these figures, analyses could be carried out in the low parts-per-billion range.

Table 5. Silicon by Graphite Furnace AAS – Analytical Results

Sample	Program 20	Si Jet oil II	Mean		
	Conc (ppb)	%RSD	ABS	ABS	Readings
Blank	0.00		0.018	0.018	0.018
Addition 1	12.50	1.9	0.094	0.092	0.095
Addition 2	25.00	1.9	0.139	0.137	0.141
Addition 3	37.50	2.9	0.179	0.183	0.175
Sample 1	11.56	6.7	0.039	0.041	0.037

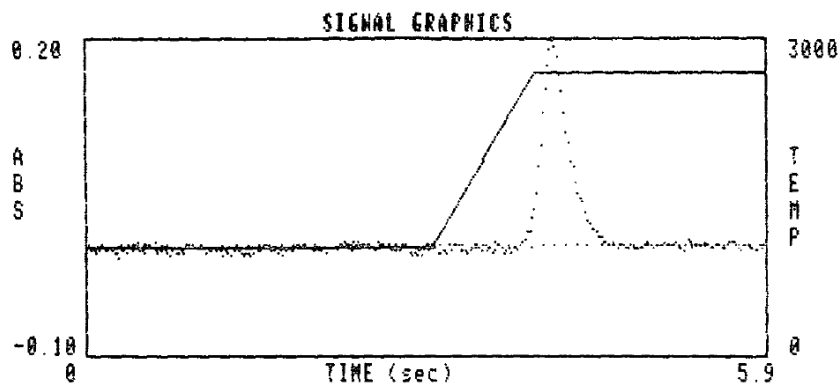


Figure 2. Silicon by graphite furnace AAS – a standard addition signal.

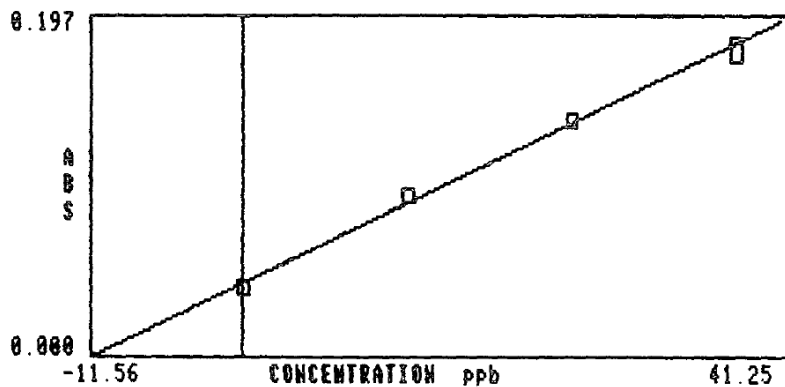


Figure 3. Silicon by graphite furnace AAS – calibration graph.

Tin in Jet-Engine Oil By Furnace AAS

The development of a method for tin by graphite furnace AAS indicated that a short dry time would be possible in the furnace program. This permitted the development of a temperature program which is complete within one minute. The possibility of background interference was thoroughly investigated, and it was found that background correction was not necessary.

An ash temperature of 800 °C was used. Above 800 °C losses of tin were detected during the program development. An atomization temperature of 2600 °C was used, as shown in Table 6.

Table 6. Tin by Graphite Furnace AAS – Furnace Parameters

Step no.	Temperature (C)	Furnace parameters			Read command
		Time (sec)	Gas flow (L/min)	Gas type	
1	40	1.0	3.0	Alternate	No
2	120	10.0	3.0	Alternate	No
3	800	30.0	3.0	Alternate	No
4	800	15.0	3.0	Alternate	No
5	800	3.0	0.0	Alternate	No
6	2600	0.9	0.0	Alternate	Yes
7	2600	2.0	0.0	Alternate	Yes
8	2600	3.0	3.0	Alternate	No

The sampler parameters are shown in Table 7. Total volume was 10 microlitres.

Table 7. Tin by Graphite Furnace AAS – Sampler Parameters

	Sampler parameters volumes (µL)			
	Standard	Sample	Blank	Modifier
Blank	–	–	10	
Addition 1	2	4	4	
Addition 2	4	4	2	
Addition 0	–	4	6	

There is no significant blank signal detected during the tin analysis. A typical standard addition peak is shown in Figure 4. The peak is sharp and well shaped.

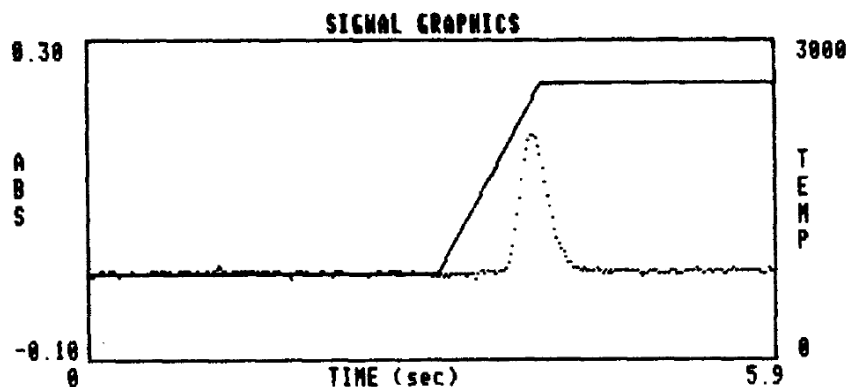


Figure 4. Tin by graphite furnace AAS – a standard addition signal.

Results are given in Table 8. Blank readings were low and the precision of the analysis was good. The additions standard was 250 ng/mL of tin. The calibration graph from this data shows a high degree of linearity over the concentration range, as shown in Figure 5.

Table 8. Tin by Graphite Furnace AAS – Analysis Results

Sample	Conc	%RSD	Program 9 Sn			
			Mean ABS	Readings		
Blank	0.00		0.009	0.008	0.010	0.010
Addition 1	125.0	2.6	0.130	0.133	0.126	0.132
Addition 2	250.0	3.3	0.218	0.221	0.224	0.210
1.	65.2	1.2	0.046	0.045	0.046	0.046

The oil sample analysis gave a result of 65.2 ng/mL of tin, indicating a concentration of 0.326 µg/mL of tin in the original oil. Such a value is considered normal by the operator of this aircraft.

The characteristic concentration derived from this data is 25 picograms. This compares favorably with the expected literature value of 50 pg for determination in an aqueous medium without a chemical modifier, or 22 pg with a modifier [13]. On the basis of these results a 10 microlitre sample of 25 ng/mL tin in oil/MIBK would give an absorbance of 0.044.

Titanium in Jet-Engine Oil by Furnace AAS

The analytical signal obtained for titanium in jet-engine oil is not a simple one. A background signal is detected during atomization which rises to a low plateau. When no sample is deposited in the tube this background level is still observed from a blank tube firing. It was established that the background was not due to a memory effect. This suggests that the background signal is caused by the removal of small amounts of graphite from the graphite tube at the high atomization temperature used for titanium, 2900 °C. Titanium and boron are the only two elements requiring such high atomization temperatures [13].

This background signal is satisfactorily corrected for as shown in the graphics trace for the blank signal in Figure 6. The low plateau of background is represented by the dotted line, while the corrected atomic signal is shown as a solid line. The peak of the titanium atomic signal tails off, as shown in Figure 7, and is rapidly reduced to zero as the inert gas is turned on after atomization. However, the atomic signal rises rapidly just before the background signal, and it has been found that a reproducible analysis is possible, even without background correction.

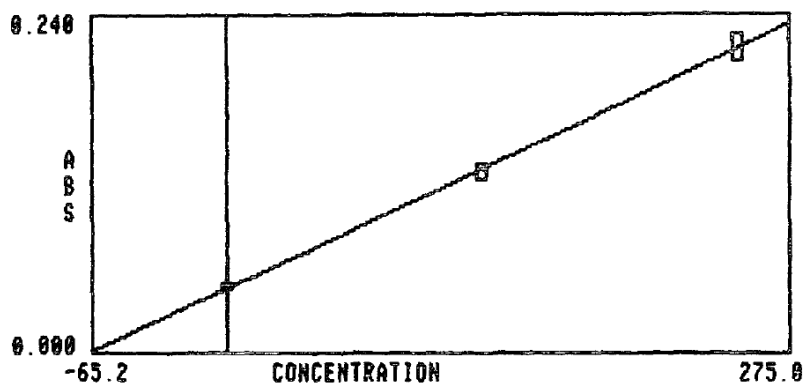


Figure 5. Tin by graphite furnace AAS – calibration graph.

A typical blank signal with the background corrector off is shown in Figure 8, and the signal from a standard addition is shown in Figure 9. The furnace parameters developed for titanium give an analysis time of less than two minutes. The furnace parameters are given in Table 9. The sampler parameters are given in Table 10. Total volume was 10 microlitres.

The results for titanium exhibit good precision (Table 11). The calibration data is presented in Figure 10.

The aircraft engine oil sample shows a result of 506.0 ng/mL, indicating an original oil sample concentration of 2.5 µg/mL. Such a value conforms to normal operational levels according to the operator of this aircraft.

The characteristic concentration calculated from this data is 110 pg, which is twice the value expected for aqueous samples [13]. A 10 microlitre volume of a 110 ng/mL Ti sample would give an absorbance of 0.044.

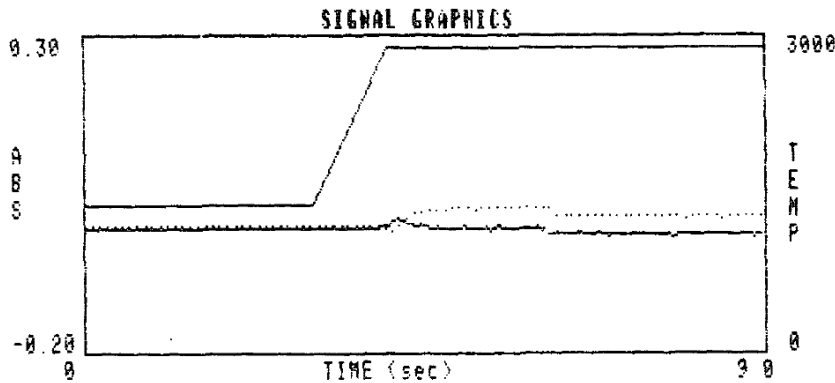


Figure 6. Titanium by graphite furnace AAS – tube background signal.

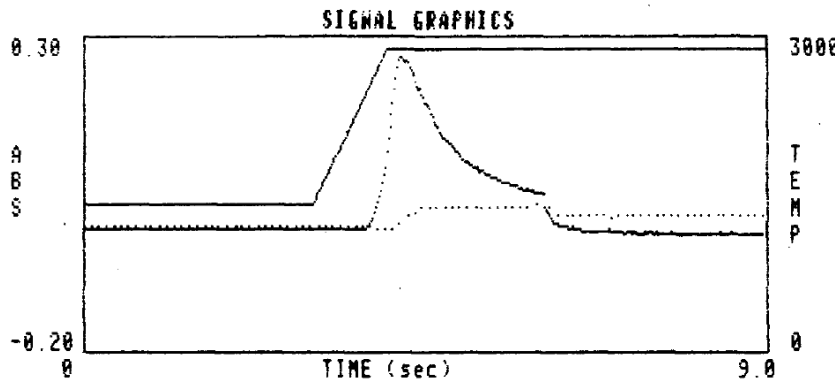


Figure 7. Titanium by graphite furnace AAS – sample background and atomic peak.

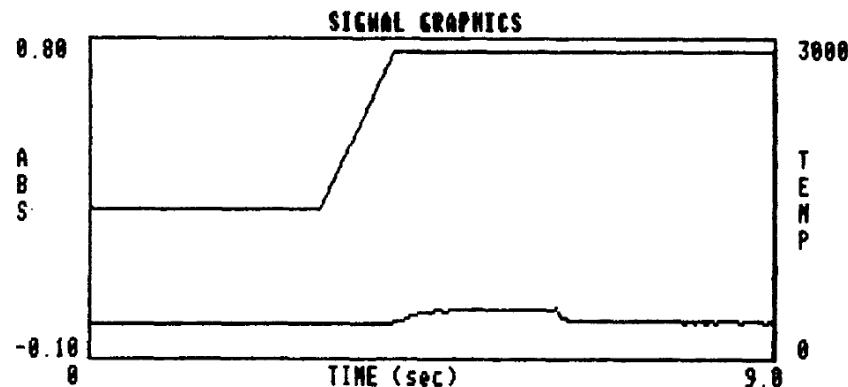


Figure 8. Titanium by graphite furnace AAS – a blank signal.

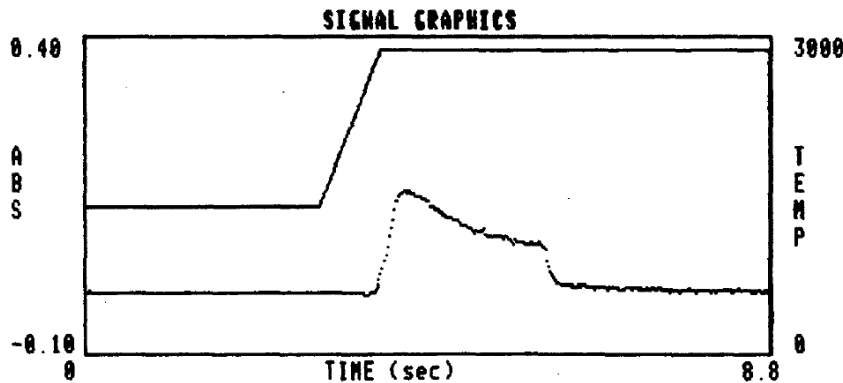


Figure 9. Titanium by graphite furnace AAS – a standard addition.

Table 9. Titanium by Graphite Furnace AAS – Furnace Parameters

Step no.	Temperature (C)	Furnace parameters			Read command
		Time (sec)	Gas flow (L/min)	Gas type	
1	40	2.0	3.0	Alternate	No
2	80	30.0	3.0	Alternate	No
3	80	10.0	3.0	Alternate	No
4	150	10.0	3.0	Alternate	No
5	1400	15.0	3.0	Alternate	No
6	1400	15.0	3.0	Alternate	No
7	1400	3.0	0.0	Alternate	No
8	2900	0.8	0.0	Alternate	Yes
9	2900	2.0	0.0	Alternate	Yes
10	2900	3.0	3.0	Alternate	No

Conclusion

Analytical programs for the measurement of silicon, tin and titanium in jet-engine oil have been developed. These programs would be suitable for the routine monitoring of wear metals for in-service aircraft, or other oil-lubricated engines or equipment. The use of graphite tube atomization AAS allows the determination of very low levels of these elements, providing convenient early warning of possible component failure. The elements investigated were chosen because of the relatively low sensitivity obtained by conventional flame AAS techniques.

Table 10. Titanium by Graphite Furnace AAS – Sampler Parameters

	Standard	Sampler parameters volumes (µL)		Modifier
		Sample	Blank	
Blank	–	–	10	
Addition 1	2	4	4	
Addition 2	4	4	2	
Addition 0	–	4	6	

Table 11. Titanium by Graphite Furnace AAS – Analytical Results

Sample	Conc (ppb)	%RSD	Mean Readings			
			ABS	0.010	0.008	0.007
Blank	0.0		0.008	0.010	0.008	0.007
Addition 1	250.0	4.8	0.120	0.114	0.120	0.125
Addition 2	500.0	2.1	0.160	0.160	0.163	0.157
1.	506.0	3.2	0.081	0.078	0.080	0.083

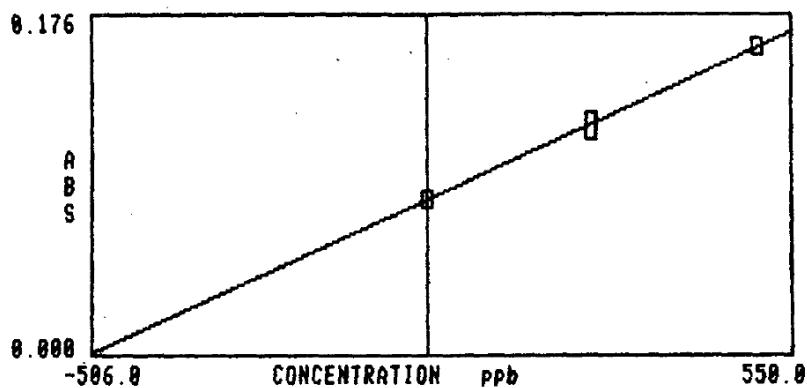


Figure 10. Titanium by graphite furnace AAS – a standard addition signal.

References

1. K. J. Eisentraut, C. S. Saba, R. W. Newman, R. E. Kauffman, W. E. Rhine, "Spectrometric Oil Analysis, Detecting Engine Failures Before They Occur", *Anal. Chem.*, **56**, 1984, pp 1086A-1094A.
2. T. McKenzie, "Atomic Absorption Spectrophotometry for the Analysis of Wear Metals in Oil Samples", *Varian Instruments at Work*, 1981, AA-10.
3. A. D. King, D. R. Hilligoss, G. F. Wallace, "Comparison of Results for Determination of Wear Metals in Used Lubricating Oils by Flame Atomic Absorption Spectrometry and Inductively Coupled Plasma Emission Spectrometry", *Atomic Spectroscopy*, **5**, 4, 1984, pp 189-191.
4. M. de la Guardia, A. Salvador, "Flame Atomic Absorption Determination of Metals in Lubricating Oils: A Critical Review", *Atomic Spectroscopy*, **5**, 4, 1984, pp 150-155.
5. C. S. Saba, K. J. Eisentraut, "Determination of Titanium in Aircraft Lubricating Oils by Atomic Absorption Spectrophotometry", *Anal. Chem.*, **49**, 1977, pp 454-457.
6. J. R. Brown, C. S. Saba, W. E. Rhine, K. J. Eisentraut, "Particle Size Independent Spectrometric Determination of Wear Metals in Lubricating Oils", *Anal. Chem.*, **52**, 1980, pp 2365-2370.
7. C. S. Saba, W. E. Rhine, K. J. Eisentraut, "Efficiencies of Sample Introduction Systems for the Transport of Metallic Particles in Plasma Emission and Atomic Absorption Spectrometry", *Anal. Chem.*, **53**, 1981, pp 1099-1103.
8. R. E. Kauffman, C. S. Saba, W. E. Rhine, K. J. Eisentraut, "Quantitative Multielement Determination of Metallic Wear Species in Lubricating Oils and Hydraulic Fluids", *Anal. Chem.*, **54**, 1984, pp 975-979.
9. C. S. Saba, W. E. Rhine, K. J. Eisentraut, "Determination of Wear Metals in Aircraft Lubricating Oils by Atomic Absorption Spectrophotometry Using a Graphite Furnace Atomizer", *Applied Spectroscopy*, **39**, 4, 1985, pp 689-693.
10. "Operating Conditions for Flame Atomic Absorption Spectrometry", *Varian Publication No. 85-100274-00*, 1983.
11. T. McKenzie, "Safety Practices Using Organic Solvents in Flame Atomic Absorption Spectroscopy", *Varian Instruments at Work*, 1980, AA-6.
12. "Varian Techtron Product Line News" No. 135, 1981.
13. "Operating Conditions for Furnace Atomic Absorption Spectroscopy", *Varian Publication No. 85-100504-00*, 1981.

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