



SOS:

SOURCES OF SILICON

by John Evans B.Sc.



John Evans

Oil analysis is a well-established condition monitoring technique that has been with us since the late 1940s. It originally developed from a need to monitor main bearing wear in locomotive engines in the United States by spectrometrically measuring the amount of lead in the engine oil. Oil analysis has come a very long way in the last 60 years with the introduction of a whole range of tests that include acid and base numbers, particle counting, infra-red spectroscopy, viscosity, water and fuel contamination and many, many more. However, spectrometric analysis still remains at the core of any oil analysis programme and provides the greatest amount of information in the shortest possible time and at the lowest cost.

Spectrometric measurement of silicon

Usually identified by the acronym SOAP or Spectrometric Oil Analysis Programme, this

technique measures the concentrations of wear metals, oil additives and contaminants in used oil samples. These concentrations are based on the elements found in the periodic table of elements that some of you may remember from matric chemistry lessons. Wear elements such as copper and iron, additives like zinc and calcium, and contaminants such as lithium and sodium are identified, and their concentrations measured.

There are several different instrumental techniques that can be employed to do this, such as atomic absorption, spark emission and inductively coupled plasma (ICP) spectroscopy – the last two techniques are the most commonly used. In most of WearCheck's laboratories, ICP spectroscopy is the preferred technique. With this instrument the oil is mixed with a suitable solvent and introduced into a plasma that has the ability to heat the sample up to nearly



A technician operates an ICP spectrometer in WearCheck's Pinetown laboratory

10 000°C, which is the same temperature as the surface of the sun. At this sort of temperature the different elements from the periodic table will emit light of different, yet very specific, frequencies (colours) and the intensity of this light is proportional to the amount of the element present in the oil. It is in this way that the amount of each wear metal, oil additive and contaminant can be measured at an elemental level.

The interpretation of oil analysis results could be made very much easier if every element measured belonged to only one category (wear metals, contaminants or additives), but oil analysis, like life, is very rarely simple. Often a particular element can belong to more than one category and occasionally at the same time. One of the elements that can belong to all three categories is silicon, and it is usually only by looking at the other results that the source of the silicon can be determined. It is important to remember that the diagnosis of oil analysis results is a holistic process and the full picture can only be seen by considering all results in relation to each other. This also explains why limit tables can often be very misleading.



WearCheck diagnostic manager John Evans shows the location of silicon in the periodic table

The discovery of silicon

Silicon is element 14 in the periodic table and found towards the upper right hand part of the table. It is a metalloid, which means that it is not wholly a metal or a non-metal but has characteristics of both groups of elements; chemically it is similar to carbon. It was first isolated in its pure form in 1824 by Berzelius but had been identified by Lavoisier in 1787. It is the eighth most common element in the universe but the second most common element in the earth’s crust after oxygen, and has a melting point of 1410°C. In its pure form silicon is crystalline and has a dull grey metallic lustre, however it is rarely found in its pure state.

Name	Silicon
Atomic number	14
Relative atomic mass	28.086
Density	2.33
Melting point	1410
Boiling point	2355
Discovered	1787
Isolated	1823

Although the ICP spectrometer measures the amount of silicon in the oil, as noted above, the element is not often found in its pure state and will usually be present in the oil combined with other elements such as oxygen. Silicon detected in oil analysis is usually in the chemical form of silicates, silicones and siloxanes; it can also be alloyed with true metals.



A small piece of pure silicon

Dirt entry

Most people familiar with the interpretation of oil analysis results will know that the presence of silicon in oil is associated with the presence of air-borne dust or dirt. Dirt is not pure silicon but silicon combined with oxygen (and other elements) to form a family of compounds known as silicates or pure silicon dioxide (also known as silica). Silicates are very common in the earth’s crust and are the major constituent of sand; quartz, mica, talc, clay and ordinary glass are also examples of silicates. Unfortunately for the oil analyst, seeing silicon in an oil sample does not always mean that dirt is present; silicon can have many other sources and this bulletin takes a look at the various sources of silicon in an oil sample and how they are identified.



A piece of quartz (silica, silicon dioxide)

Dirt, sand, soil, air-borne dust or whatever you want to call it is not purely made up of silicon dioxide, but contains many other compounds that constitute a complex mixture. One of the other most common constituents of dirt is aluminium trioxide and invariably, if dirt is getting into a lubricated system, aluminium will be identified along with the silicon. Also remember that dirt is highly abrasive so an increase in general wear readings would be expected along with an increase in both silicon and aluminium. The ratio between aluminium and silicon varies, but typically that ratio (Si:Al) should be between 4:1 and 2:1. So, in order for the source of silicon to be due to dirt, a definite increase in aluminium would be expected along with wear elements such as iron, chromium, lead and copper. If silicon increases but there is no increase in aluminium, it is highly unlikely that the source of silicon is from dust.

There is an interesting corollary to this in that dirt entry will depend on what sort of 'dust' is in the environment; in the vast majority of cases this will be a mixture of silicon and aluminium oxides but not always. In areas where ores and minerals are mined it is quite possible that these elements may show up as dirt entry rather than the traditional silicon and aluminium. It is not uncommon to see zirconium and titanium in earthmoving equipment working in Richards Bay or manganese in gearboxes at a Samancor mine. Chromium is sometimes seen in areas around Steelpoort. It is only by looking at the ratios of the various elements that it is possible to determine if a high chromium reading is due to dirt entry or bearing wear. A high degree of diagnostic skill coupled with a vast amount of experience is required to make these very fine distinctions.

Now let us look at other possible sources of silicon that can show up in an oil analysis report.

Internal coolant leaks

The cooling system in water-cooled lubricated systems such as transmissions, engines and gearboxes obviously contains water, but the water also has a coolant conditioner that allows the water (coolant) to perform at its best. This package of chemicals is used to raise the boiling point, lower the freezing point, limit rust and corrosion, reduce the amount of cavitation occurring and prevent chemical attack of certain metals. Part of this additive package may contain chemicals that contain silicon.

When an internal coolant leak occurs, water can leak from the water side of the cooler into the oil side. Often this water will evaporate at working pressures and temperatures so it is not detected in the oil analysis results, however, the chemicals that make up the coolant additive package get left behind in the oil and one of the elements that can get left behind is silicon.

So, how can you tell if the elevated silicon is due to dirt or an internal coolant leak? Firstly, it is unlikely that the aluminium will be elevated and secondly, other chemicals found in the cooling water will also be found in the oil - most commonly sodium but also other elements found in the coolant additive package such as boron and molybdenum. A word of caution needs to be made however, as sodium, boron and molybdenum are also found as part of the oil's additive package. Again it is only by looking at the full set of results holistically that the origin of the various elements can be determined.

Sodium metasilicate, also known as water glass, can be added to cooling systems to prevent leaks.

The oil's own additive package

Industry has been made more aware of the damage that dirty oils can do to mechanical equipment; 75% of all premature failures of hydraulic systems are due to particulate contamination and some sources put that percentage even higher. As a result of this increase in awareness of the damage that dirt can do, companies that use large quantities of oil and have bulk storage on site, test their oils on a regular basis for cleanliness. Much to their horror, most new oils have a silicon level usually between five and fifteen parts per million.

This is not dirt as, once again, there will be no aluminium present, so that pretty much rules that source out. The silicon is actually due to a chemical that is part of the additive package of the oil. Going under the rather grand chemical name of polymethylsiloxane, this chemical is added to the oil, in trace amounts, to retard the effect

of foaming when oil gets churned around during application.

The additive does not actually prevent foaming but is a surfactant that ensures that any foam that forms will collapse quickly as it interferes with air/oil interface. Similar additives are added to fuels in formula one racing so that the cars' fuel tanks can be filled very quickly during a pit stop without foaming occurring.

So there is no need to panic, the 10 ppm silicon you see in your oil is not dirt but part of the oil's additive package – it is supposed to be there.

One of the most important ways of assessing unused oil cleanliness is to carry out a particle count and determine the ISO 4406 cleanliness code. This measures the number of particles per millilitre of oil in a variety of size ranges from around four up to 100 microns. This allows oil companies, OEMs and end users to set, measure and maintain cleanliness targets. Interestingly, the anti-foaming additive can have a marked effect of the particle count data. In high concentrations the additive can form what are known as micelles. These are additive molecules

do perform specific functions in industry. Silicone lubricants are extremely resistant to oxidation and are often used in compressors that compress oxygen where the threat of fire and explosion is very high. They do need to be used with caution as they are not compatible with most other lubricants and additive solvency is also a problem. These fluids are easily identified by their incompatibility with laboratory solvents and the presence of silicon in the thousands of parts per million.

Silicone-based gaskets and sealants

Another source of silicon that can introduce very high levels of the element into the oil is from silicone-based sealants and gasket compounds. During assembly or repair, silicone-based gasket compounds may be used. These come into contact with oil and leach into the lubricant, resulting in readings of several hundreds of ppm but there is no need to worry, this is not a case of the gasket dissolving, simply some of the compound ending up in the oil. Fortunately these cases are quite easy to identify, which is useful in that they occur fairly often. Again, as no dirt is involved, the aluminium does not increase and generally the wear readings are quite low and no sodium is involved

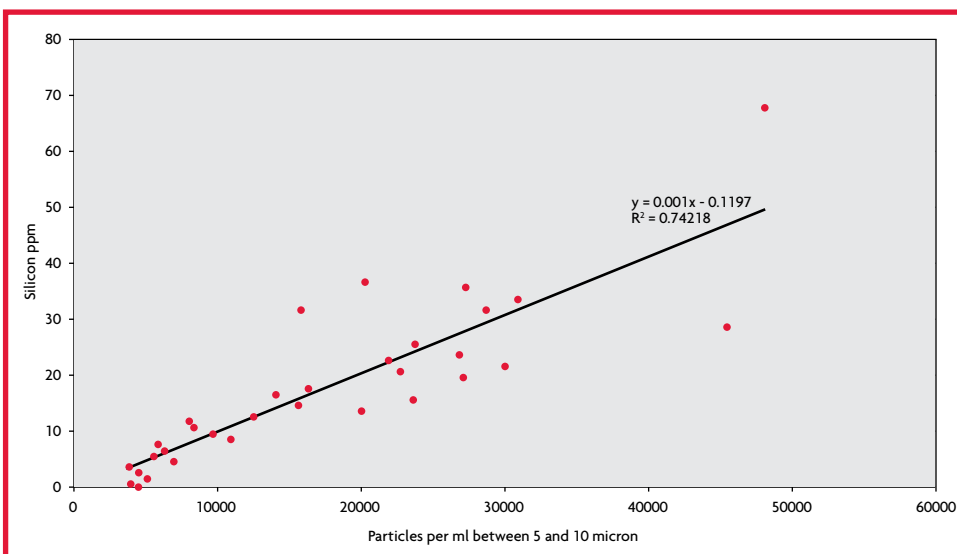
either. What shows up is a very high silicon level with no other apparent disturbance in the other readings.

Silicone sealants that leach into clean oil systems can have the same effect on particle count data as anti-foaming additives.

Silicon as a wear element

Silicon is usually alloyed with aluminium in the construction of pistons, thus making it a wearing element as well as an oil additive, base stock and

contaminant from a variety of sources. Alloying aluminium with silicon enhances the metal's castability to produce lightweight, durable and corrosion-resistant components. The total amount of silicon that can dissolve in aluminium is around 12%, however, alloys containing 14% to 19% are produced, which results in what is known as a hypereutectic piston. This dramatically reduces the coefficient of expansion of the piston as it heats up, thus allowing engineers to design engines with higher tolerances.



The graph shows the relationship between silicon levels and particle counts in unused oils

which, when grouped together are big enough to be counted by some types of particle counting instruments. The graph above shows the relationship between silicon levels in unused oils and the four to six micron particle count data.

Silicone-based fluids

Following on from silicon being part of the additive package, it can also be part of the make up of the oil's base stock. Silicone-based oils are very rare but

Vehicle: 5263 - ENGINE - Alt. ID: - -

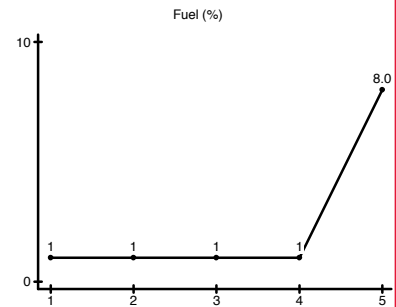
SAMPLE NUMBER	DATE SAMPLED	LAB DATE	OIL CONSUMPTION	SMR	UNITS	OIL IN SERVICE	FILTER CHANGE	OIL DRAIN	RRI	
1	W329488	28.09.09	30.09.09	-	101463	KM	4000	No	No	10000
2	W441032	06.01.10	15.01.10	-	115971	KM	4000	No	No	10000
3	W777183	27.10.10	10.11.10	-	13886	KM	4000	No	No	10000
4	WH86616	28.11.11	02.12.11	-	68389	KM	4000	Yes	Yes	10000
5	WH38856	12.12.11	30.12.11	-	19049	KM	-	No	No	10000

WEAR METALS

Sample	Iron	Chromium	Nickel	Molybdenum	Aluminium	Copper	Tin	Lead	PQ Index
1	5	1	0	0	2	3	0	0	7
2	19	1	1	11	5	9	0	3	11
3	24	0	0	4	5	4	1	4	13
4	32	3	1	2	12	6	0	9	15
5	88	3	6	3	360	13	0	18	2493

30 spectrometric analyses are carried out on all samples but only relevant results are reported in parts per million.

FUEL

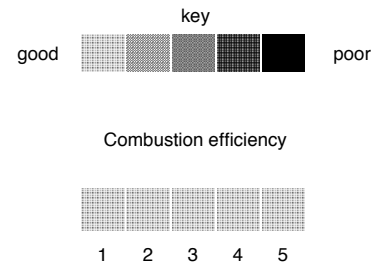


CONTAMINANTS

Sample	Silicon	Sodium	Manganese	Soot Value	Soot %	Oxidation	Sulphate	Nitrates	Fuel (%)	Water (%)
1	2	7	0	0	0.0	13	22	6	<1	ND
2	5	11	1	3	0.1	16	22	9	<1	ND
3	5	9	0	20	0.4	14	23	8	<1	ND
4	14	7	0	19	0.4	12	18	11	<1	ND
5	73	5	2	11	0.2	13	20	6	8.0	ND

30 spectrometric analyses are carried out on all samples but only relevant results are reported in parts per million.

COMBUSTION

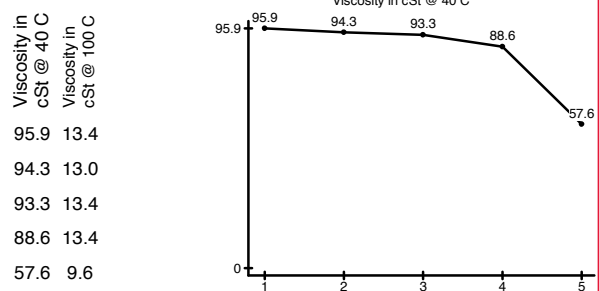


ADDITIVES & LUBRICANT CONDITION

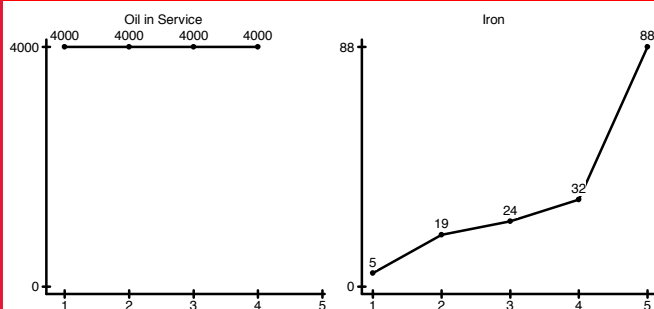
Sample	Magnesium	Calcium	Zinc	Phosphorous	Barium	Boron	Sulphur	TBN
1	10	2866	1292	1100	0	2	8716	+6
2	13	2745	1171	993	0	7	9182	+6
3	11	3289	1344	1235	0	17	7408	+6
4	23	4318	1263	1121	1	234	4741	+6
5	15	1798	774	774	0	67	6700	3.8

30 spectrometric analyses are carried out on all samples but only relevant results are reported in parts per million.

VISCOSITY



GRAPHICAL REPRESENTATION OF KEY DATA



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Requested by johne

An oil analysis report illustrating piston torching - note the silicon, aluminium, PQ and fuel readings

The amount of silicon present in the piston is usually too small to be detected as a wearing element during the normal course of events; 25 – 50 ppm aluminium might be considered high but would only release less than ten ppm silicon into the oil, which is down around the level of the anti-foaming additive in the oil.

Under exceptional circumstances, a phenomenon known as piston torching can take place. The occurrence in itself is not that rare, but because it leads to a sudden death failure, it is rarely detected by oil analysis. If, however, there is an injector with a faulty spray pattern that allows diesel to lie on top of the piston and burn the piston, torching will take place. If such a situation arises just (literally, minutes) before an oil sample is drawn, then the evidence of piston torching will be present in the oil.

High levels of aluminium will be present as would be expected, but there will also be a disproportionate amount of silicon evident. This may be confusing, as elevated silicon and aluminium levels would normally be sure signs of dirt entry; however, in this case the ratio of the two elements will be distorted by the silicon present in the piston. Ratios of Si:Al of 1:1 can be seen, and often there is more aluminium than silicon. With a bit of luck some of the unburned fuel will get into the sump and be detected by oil analysis thus clinching the diagnosis, and visible aluminium particles will be present in the oil.

A final assessment

Oil analysis, like life, can get very complicated - there are surprisingly few simple answers to what appears to be simple problems. Most people like a straightforward answer when asking a straightforward question, but in oil

analysis a lot of questions have multi-factorial answers. This bulletin shows how just one element from the many individual test results that can be determined on an oil sample can either be vegetable, animal or mineral, and possibly all three at the same time; and silicon is not the only parameter to which this kind of treatment can be applied.

Readings cannot be looked at in isolation and it is sometimes only by comparing ratios of a variety of readings that an accurate assessment of the oil analysis results can be made. Simply saying that a silicon level up to 15 ppm is okay, 15 to 30 ppm is actionable and over 30 ppm is serious, is not a realistic way of diagnosing an oil sample.

It is only by looking at all the results in a holistic manner, including the ratios of one reading with others, comparing histories and taking into consideration all the data supplied by the customer, that a true picture of what is actually going on in a lubricated component can be obtained.

As already mentioned, this takes a high degree of diagnostic skill and a vast amount of knowledge that can only be gained through many years of experience and the diagnosis of literally millions of samples.

WearCheck's diagnostic team consists of seven diagnosticians, including graduate and diplomate engineers and chemists, with a combined diagnostic experience of more than 120 years and six million samples.

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