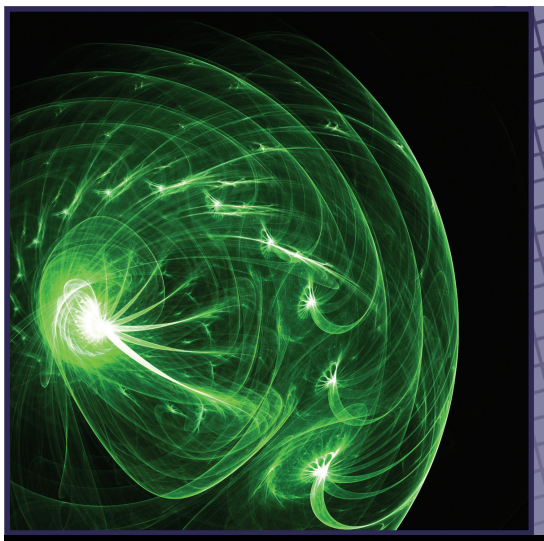

Reduced Volume TAN System Saves Cost and Use of Organic Solvents

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In a presentation given during Pittcon 2012,* (Session 2035 –Fuel Analysis), Trevor Blows, Application Chemist, of GR Scientific, described a new micro system for TAN Analysis which operates with a reduced solvent volume requirement, bringing associated cost savings and environmental benefits. This article looks at how this system was developed as a different approach to meeting customer needs.

Introduction -What is TAN

Oils continually react with atmospheric oxygen to produce organic oxidation products that are acidic in nature. At ambient temperature, this reaction is very slow and has little effect upon oil conditions. At the elevated temperatures that exist within an operating engine, reaction rates are much higher. Elevated operating temperatures can generate high levels of weak organic acids. They cause increased oil viscosity and can deposit as lacquers on hot surfaces.

Total Acid Number or TAN is the measure of both the weak organic and strong inorganic acids present in oil. It is applicable to gearbox, gas engine, gas turbine and hydraulic lubricants. It is an important quality measurement of crude oil. The TAN value indicates to the crude oil refinery the potential of corrosion problems. Total Acid Number is an analytical test to determine the deterioration of lubricants. The more acidic a lubricant is, the further its degradation has proceeded.

Features

Following a consultation period with customers GR Scientific developed and refined a micro system for Total Acid Number (TAN) analysis which incorporates a newly developed micro combination pH electrode and optimised titration vessel. Providing for enhanced health and safety in use and also meeting environmental impact considerations, the newly introduced Aquamax MicroTAN system has been shown to save up to 75% of the volume of organic solvent used in analysis, reducing cost per test to around $2, while also bringing down costs of waste solvent disposal.

Conforming to ASTM D 664-09: Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration - the analyser has been developed specifically for the wide range of TAN values expected from oil industry samples.

Electrode performance check for ASTM D664-09 compliance

- The D664-09a recommends the use of aqueous buffers to check electrode performance and to determine the TAN titration end point when no definite point of inflection is obtained.
- The basic manual system described in the ASTM text is a mV meter (or pH meter with mV mode). It measures electrode performance/Nernstian slope efficiency in aqueous pH 4 and 7 buffers. The electrode system is then conditioned to measure the mV response of non-aqueous oil samples. This is the basis of the TAN test.
- The measurement of electrode performance/Nernstian slope efficiency is not part of the TAN test. It only ensures that the electrode system is functioning correctly before being used for the non aqueous titration.
- The GR Scientific micro system is used for TAN measurement. It uses the mV reading taken from a pH11 buffer as the end point for the TAN titration. The system does not measure Strong Acid Number so the use of pH4 calibration is not required.
- D664-09a Appendix X1, is a non mandatory check for electrode performance. It is noted that X1.1 states that 'a manual check can be carried out with a pH meter or titrator with mV reading capability'. So D664-09a does allow the use of a pH meter to check electrode performance.

How it works

The system, designed for ease of use, is calibrated using aqueous pH11 buffer and the blank value for the titration solvent determined. This value is stored automatically for use in later TAN calculations. Following titration the results, expressed as mg KOH/g, are displayed on the screen and stored in the data logger. Printer or PC options are available and can be configured to suit user requirements.

Micro system development – why?

During meetings and demonstrations with companies in the UK and Northern Ireland during 2010, it became apparent that existing technology was no longer addressing some of the users' needs. Common issues raised by customers included :-

'Macro System works well but we spend a lot of money on solvents'.

Budgets were being reviewed.

High cost to dispose of organic solvent waste.

Health and safety issues.

"Surely you can reduce sample volume?"

Setting out to address these changes GR Scientific tested the analytical system with a customer using glass vessels resulting in 40mL capability. This was reduced further to 25mL with the development of a micro combination pH electrode. Further trials went well with the customer adopting the system almost immediately and it is now in regular use.

Electrode selection and development

Key to the success of the instrument has been the electrode technology. GR Scientific worked closely with a UK sensor company to develop a micro combination electrode.

It provides:

- Excellent stability for non-aqueous titrations.
- An easy to clean design which is an important feature necessary for oil analysis systems.
- Regeneration to optimum efficiency in minutes.
- Electrode designed to meet titration vessel geometry.
- Minimised effect from stirrer vortex.

Case studies

The following case studies indicate how the Aquamax MicroTAN compared with other methods of analysis.

Engine oils

At the elevated temperature of operation within engines, high levels of acid are generated. The acid increases oil viscosity, causing reduced efficiency and damage to the exposed engine parts. The TAN value assists service operations by giving an indication of oil change requirements.

A customer using traditional methods of TAN analysis wanted to compare results against the micro TAN titrator. The results were consistent with that of the customer.

Details are given below.

Engine oil: expected TAN 3.4

Weight (g)	Titre (ml)	TAN result
0.51	0.497	3.36
0.51	0.510	3.51
0.50	0.515	3.63
0.52	0.510	3.44
0.50	0.508	3.56
0.50	0.482	3.26

Transformer oils – optimised method

After discussions with customers analysing transformer oils, it was decided to spend time optimising the method for these sample types.

Typically, samples have the same, known density, of 0.875. It follows that 1mL of sample weighs 0.875g. A fixed volume of sample can be put into the titration vessel using the calibrated syringe, optimised for coloured samples. The weight of the sample can be keyed into the titrator. (at 0.875g per mL of sample).

The titration is then started. At endpoint, the result is read directly on the display.

A number of samples were run. The system was standardised with a known solution. Good correlation was achieved.

UK transformer oil data

Sample	Weight (g)	Titre (ml)	TAN result
Low TAN 0.06 expected	5.63	0.283	0.092
Low TAN 0.06 expected	5.81	0.301	0.107
Low TAN 0.06 expected	5.91	0.298	0.102
MXN 0.17	8.17	0.532	0.234
MXN 0.17	6.40	0.474	0.248
STAN 2	5.63	2.013	1.950

Lubricant sample

Another UK customer has used the colorimetric method of analysis of lubricants for many years. As part of a laboratory upgrade scheme, the customer needed to assess the micro TAN system for his samples. The sample gave good, accurate results. These were slightly higher than those achieved with the colorimetric method. However it does show the limitations of the colorimetric method whose endpoint is determined by visual colour comparison against a standard colour chart.

UK lubricant sample: expected TAN 0.8 (customer colorimetric result)

Weight (g)	Titre (ml)	TAN result
1.16	0.408	1.05
1.00	0.353	0.91
1.01	0.391	1.11
1.00	0.391	1.12
1.00	0.371	1.01
1.00	0.371	1.02

These results do show the accuracy provided by automatic titration systems compared to the traditional colorimetric methods. The importance of the TAN parameter to the performance of lubricant and transformer oils cannot be understated. The performance of engines and transformers are key to many industries. An optimized system that offers costs savings and health and safety benefits, while maintaining high performance is a great addition to the oil analysis laboratory.

ASTM D664 method for TAN

- ASTM D 664-09 Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration.
- Sample is titrated with 0.1mol/L potassium hydroxide 2-propanol solution and the endpoint is determined on titration curve.
- Result is calculated from titration volume of potassium hydroxide/ 2-propanol solution reaching the endpoint.
- The Total Acid Number (TAN) result is given as the amount of potassium hydroxide in milligrams that is needed to neutralize the acids in one gram of oil.

Low level TAN values

There are also many customers analysing samples for TAN values below the limit of ASTM D664-09. The problem with the standard micro system in this case is that the titre values are very small in comparison to the solvent blank values. One way to approach this issue is to use a reduced molarity titrant. For low level TAN values, the reduction of the KOH strength to 0.01M gives workable titre values. Samples from the UK and USA were analysed and consistent results achieved. This does increase the scope of the micro TAN analyser for very low acid levels in oil samples.

Key features

- Conforms to ASTM D 664-09
- Very easy to use with intuitive keypad and function guide display.
- Automatic data storage of last 55 analysis results.
- 10ml high precision syringe featuring 40,000 stepper motor.
- Connects to external PC keyboard for easy text and sample information data entry.
- Connects to different types of printers, PC and balances.
- 2 x RS 232C sockets for printer/PC/balance connection.

Examples:

US sample

10 – 12g was taken and a 'more workable' titration volume of 0.85mL was given. Results of 0.034, 0.032 and 0.035 show the sensitivity and accuracy of the unit.

UK transformer oil with very low TAN value

12 – 15g of sample was taken and gave a titration volume of 0.3mL. With a standard system, a large weight of sample, and corresponding large volume of solvent, would be needed to get even the smallest titre above the blank value. Excellent results of 0.005, 0.004 and 0.005 were given.

North Sea crude oils – preliminary data

Work has just started to evaluate the system for crude oil samples.

Early results from the North Sea samples are promising but more data from different crude oils is needed to prove the system.

Sample	Weight (g)	Titre (ml)	TAN result
Crude 1	0.11	1.077	3.97
Crude 1	0.14	1.301	4.02
Crude 2	0.12	1.896	7.40
Crude 2	0.08	1.241	6.60

Future development and evaluation work

Further work on varying crude oil sample types is required to prove the system. At present just two samples have been analysed but early results are promising. The technique could also be developed for additional parameters such as Total Base Number (TBN). The application to TBN analysis would give the same benefits to the customer as the micro TAN system. Finally, the micro approach could be utilised in future product development by GR Scientific, ensuring that all customers could benefit from reduced solvent use, reduced budget spend and enhanced health and safety considerations.

Summary

Conforming to ASTM D664-09 standards the Aquamax MicroTAN incorporates new technology in the form of a micro combination pH electrode and an optimised titration vessel

Applicable to petroleum products, lubricants and transformer insulating oils; new & used petroleum products; biodiesel and biodiesel blends, it has been shown to reduce use of organic solvents; reduce cost of waste disposal; offer improved analytical precision and accuracy; offer enhanced health and safety benefits and bring overall savings to budgetary spend.

*PittCon 2012, Orlando, USA, Wednesday March 14th