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PROCEDURE FOR WATER ANALYSIS OF HYDRAULIC FLUIDS USING THE KARL FISCHER APPARATUS

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by

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ABSTRACT

A Metrohm automatic Karl Fischer titrator has been used successfully for about three years in the Canadian Explosive Atmospheres Laboratory for measuring the water content of fire-resistant hydraulic fluids. The water content is critical for maintaining the fire-resistance of these fluids. The report describes the method, apparatus and procedure to be followed. A detailed analysis of possible errors is provided.

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DOSAGE DE L'EAU DANS LES FLUIDES HYDRAULIQUES À L'AIDE DE L'APPAREIL DE KARL FISCHER

par

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RÉSUMÉ

Pendant trois ans environ, on a utilisé dans le Laboratoire canadien de recherche sur les atmosphères explosives un titremètre automatique Metrohm pour déterminer, par le méthode de Karl Fischer, la teneur en eau des fluides hydrauliques résistants au feu. La teneur en eau est un paramètre très important pour ce qui est du maintien de la résistance au feu de ces fluides. Dans le rapport, on décrit la méthode, l'appareillage et le mode opératoire à suivre. On fait une analyse détaillée des erreurs possibles.

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MOTS CLÉS: fluides hydrauliques, résistance au feu, dosage de l'eau

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INTRODUCTION

Hydraulic fluids are used extensively in underground mine equipment. Because of darkness and limited means of escape, a fire in an underground mine can be a serious event. Therefore, many jurisdictions require the use of a "fire-resistant" hydraulic fluid (FRHF) rather than the usual mineral oil. The U.K. and Europe have four categories of FRHF(1): HFA - oil-in-water emulsions, HFB - water-in-oil emulsions (often called invert emulsions), HFC - glycol/water solutions and HFD - synthetic fluids (non-water containing). For the first three categories, the fire-resistant properties arise essentially from their water content. In fact, Germany specifies that the water content for HFA, HFB and HFC be at least 80%, 40% and 35%, respectively (2). Hence, it is essential that there be a means of measuring the water content.

The National Coal Board Specification (1) requires that the Dean and Stark distillation method be used for water-in-oil emulsions. The disadvantage of that method is that some water-soluble compounds are distilled over at the same time as water, yielding an apparent water content significantly greater than the actual. The same specification requires that the Karl Fischer titration method be used for water gylcols. The U.S.A. Mine Safety and Health Administration uses the Karl Fischer method for laboratory measurements of the water content of all water-containing hydraulic fluids (3).

After investigation of some alternatives, it was decided to use the Karl-Fischer method for determining the water content of hydraulic fluids submitted for certification and quality control, as well as for some research studies. An automatic titrator (Metrohm/Brinkmann) was purchased and placed into use in 1986. It has been used successfully since then. This report describes the apparatus and specifies the procedure to be followed, as well as possible errors that may be made. It should be noted that this equipment is suitable only for the laboratory and not for field use.

METHOD

The Karl Fischer reaction is the oxidation of sulphur dioxide by iodine in the presence of water, pyridine (Py) and methanol, according to the following equation:

$$SO_2 + I_2 + H_2O + 3\ Py + CH_3OH = 2\ Py{\cdot}HI + Py{\cdot}HSO_4CH_3$$

Karl Fischer reagent is a mixture of SO_2, I_2, Py and CH_3OH. Various companies sell various proprietary modifications of the Karl Fischer reagent. CEAL uses "Hydranal Composite 5", made by Eugen Scholz, which contains imidazole in place of pyridine and diethylene glycol monomethyl ether instead of methanol.

The Karl Fischer reagent is titrated into the solution which contains the unknown percentage of water. Usually, the determination of the end-point (the quantity of reagent which is just enough to react with the water) is determined electrolytically. A constant small current flows through the solution between two platinum electrodes. The potential across the electrodes drops suddenly when there is excess iodine present (i.e. just past the end-point).

APPARATUS

The apparatus consists of a Model 633 automatic Karl Fischer Titrator, a Model 655 Multi-Dosimat, a Model 649 Magnetic Swing-out Stirrer, a titration vessel, and a double platinum electrode.

The Model 633 is the part that controls the titration. A meter, which is marked EP (= end-point) on the left-hand side, provides a visual indication of the progress of the titration. Two other switches control the "time delay". The reaction is not instantaneous: the time to allow for completion of the reaction depends on the particular solution; therefore, the appropriate time delay must be set by the operator for each case.

The model 655 contains a 1-L amber bottle for the Karl Fischer reagent, a 20 ml motor-driven burette, a digital display of the volume, and controls. The volume is displayed to the nearest 0.01 ml to a maximum 99.99 ml, although the reagent is dispensed in increments of 0.002 ml. The "mode" switch provides a choice of 8 different ways of operating the burette; only mode 1, continuous addition, is useful for the application described in this report. The "0000" switch allows zeroing the display. The "dosing/filling" switch allows manual override for filling the burette (down arrow) and dispensing (up arrow). The "dV/dt" dial allows setting of the dosing speed (slowest is 1, fastest is 10). The actual dosing speed varies during the titration, fast at the beginning and slow near the end-point, in order not to overshoot. The suitable setting for most of the work is 2 - 3.

The magnetic stirrer has an off-on switch and a variable speed control. Several different titration vessels are available. The one found most convenient was EA875-200TDS, which has a side-arm stopcock for draining the vessel. In this way, the vessel need not be removed very often, at a considerable savings in time.

The lid of the titration vessel has an entry port for dispensing the Karl Fischer reagent from the burette, a port for the platinum electrodes and a septum port for injecting liquid samples. There is also a port connected to a tube filled with sieve molecular sieve that is open to the atmosphere at the other end. When the spent solution is drained from the titration vessel, air must be drawn into the vessel. Changes in atmospheric pressure also force air into or out of the vessel. It is critical that any air entering the vessel be completely dry, because the reagent reacts with any water present in the vessel, whether in the liquid or gaseous phase.

The storage bottle of Karl-Fischer reagent also contains a drying tube for the same reasons. Indicating material is added to the molecular sieve in order to know when it is no longer functional. The indicator should be bright blue; if it is pink, then the material needs to be changed. It may be regenerated by drying in an oven at 100°C for several hours until the indicator turns bright blue again and then allowing to cool to room temperature in a desiccator.

HAZARDS AND SAFETY PRECAUTIONS

Although the Hydranal reagent does not contain pyridine, it does contain compounds that are harmful when breathed or absorbed through the skin. Therefore, when handling Hydranal (e.g. filling the storage bottle), use rubber gloves and the chemical filter mask with face shield. Plan the work out so that the containers are open for as short a time as possible.

The hydraulic fluids are usually non-toxic. However, some people may be sensitive to some of them and get skin rashes. Vinyl or rubber gloves may be desirable in those cases.

The spent liquid is much less hazardous than the Hydranal. However, it may be toxic and therefore should be collected in a plastic drum for disposal by the CANMET safety group.

Syringes should be handled with care. The used needle should be broken in the Destruclip.

The usual rules of chemical laboratories apply. Lab coats and safety glasses with side shields should be worn. Personnel should not eat or drink there and wash thoroughly before leaving.

POSSIBLE SOURCES OF ERRORS IN THE METHOD

The readout on the apparatus is volume; whatever is in the burette, whether it be the proper reagent or just air, is measured. Air bubbles arise from allowing the level of reagent in the amber storage bottle to fall too low. The result will be that the measured values of percentage water will be higher than the actual. The remedy for air bubbles being present in the system is to fill the storage bottle, fill the motor-driven burette and then dispense that volume, i.e. waste it. Provided that the connections are kept tight and that the storage bottle is not emptied, this error will not occur.

The accuracy of the electrodes depends on the solution being well-stirred. The speed of the stirrer must be adjusted for different levels of liquid in the titration vessel so that a substantial vortex is formed without splashing.

Leakage of air, particularly humid air, can cause significant error. The rubber septum should be changed after every 20 - 50 injections, to prevent leakage. The molecular sieve should be regenerated as required (see above). A small amount of silicone grease is required on the electrode fitting. The O-ring on the titration vessel should be checked occasionally. Despite all these precautions, it is normal that traces of water enter the vessel over a period of time. This should require less than 0.002 ml of Hydranal/minute.

The titration vessel will need cleaning only very occasionally, when there is a considerable amount of solid material in it. (An increase of time required to reach the end-point is a good indicator that it is time to clean.) After disassembling and cleaning, it should be rinsed a couple of times with small amounts of Karl Fischer grade methanol, which contains a very low concentration of water. After putting enough methanol in to cover the bottoms of the electrodes and reassembling, at least 2 hours of titration is required to remove all traces of water in the titration vessel.

Syringe handling requires some practice to prevent errors. Since very small amounts of liquids are involved, it is critical that not even the smallest drop of liquid is lost. After a sample is drawn into the syringe, the plunger is pulled back slightly so that the contents will not be near the end of the needle where they may leak out. No attempt is made to empty the syringe completely, because there is always some liquid that will adhere to the walls. The quantity of liquid added to the titration vessel is measured by weight (difference before and after), rather than by volume, in order to have adequate accuracy.

The quantity of hydraulic fluid to be injected should be in the range of 50 - 150 mg. (This is based on the concentration of water being in the range of 35 - 45 %.) Smaller quantities of fluid would cause a larger scatter of results because of the smaller volume of titrant required. Larger quantities of fluid would require longer times to reach the end-point.

The most difficult problem is to ensure that all the water present reacts with the reagent. True solutions, such as water/glycol hydraulic fluids, present no problems. The titration time is of the order of 2 - 5 minutes. On the other hand, titration of invert emulsions requires that the emulsion be broken. This process may be assisted by increasing the stirrer speed. The titration time taken is of the order of 30 - 60 minutes. (Note that the instrument is automatic; the analyst is free to do other work during the titration.) In some cases, it may be necessary to allow the mixture to stand (with the stirrer operating) and titrate again after, say, half an hour. If the volume of the second titration is significant, or the end-point is reached too slowly, propanol or chloroform should replace part of the methanol used as the solvent.

Sampling, especially of emulsions, can be a source of large errors. After standing for a period of time, some invert emulsions tend to have an oil layer on the top and a water layer on the bottom. Furthermore, although it can not usually be seen, the emulsion layer itself may have water content increasing from top to bottom. Hence, it is vital that the container of fluid be thoroughly shaken before a sample is taken.

To reduce the possibility of gross errors occurring, it is recommended that at least three trials be carried out on each sample. The standard deviation from these trials should be in the range of 0.3 - 0.8 % water. A larger standard deviation may mean that the fluid is not sufficiently uniform, or that one of the other errors discussed above has occurred.

CONCLUSIONS

The Metrohm Karl Fischer apparatus has been in use at CEAL for about three years. Numerous water determinations have been carried out on both water/glycol and invert emulsion type hydraulic fluids. The procedure given in the appendix will yield data sufficiently accurate for the various purposes of CEAL: verify the manufacturer's specification on submitted samples, explain abnormal fire tests, carry out quality control on certified products, and conduct research into improved methods of determining stability and fire-resistance.

The difficulty with titrating invert emulsions may be the reason why the NCB specify the Dean and Stark distillation method for emulsions and the Karl Fischer method for glycol/water hydraulic fluids. With the automatic titrator, however, it is not time-consuming (in terms of actual operator attention) to check on the accuracy of the end-point, therefore the Karl Fischer method should be used for all water-containing hydraulic fluids.

REFERENCES

1. National Coal Board Specification No.570/1981 "Fire resistant fluids for use in machinery and hydraulic equipment"; National Coal Board, London, 1981.
2. German Standards: VDMA 24 317 (1982) and DIN 24320 (1985).
3. B. Conlin, U.S. Mine Safety and Health Administration, personal communication, 1985.

APPENDIX

PROCEDURE FOR WATER ANALYSIS OF HYDRAULIC FLUIDS

Set-up

1. If necessary, fill the amber storage bottle with Hydranal, using the glass funnel. Use rubber gloves and breathing protection.
2. If the titration vessel requires cleaning:
   (a) drain the vessel completely and pour the spent solution into the drum for waste;
   (b) unlatch the top part of the titration vessel and raise it by pressing the lever holding it to the stand;
   (c) clean the vessel;
   (d) rinse the vessel twice with a small amount of Karl Fischer grade methanol;
   (e) carefully wipe the electrodes;
   (f) add enough Karl Fischer grade methanol to just cover the bottom of the electrodes;
   (g) put the magnetic stirring bar into the vessel;
   (h) lightly grease the electrode fitting and the O-ring with silicone grease;
   (i) lower the top part of the vessel carefully and latch into place.
3. Turn on the power to the Model 633 and the Model 555 (a pushbutton is located on the back).
4. Turn the speed control of the magnetic stirrer to its lowest setting, turn the stirrer power on, then gradually increase the speed until a vortex is formed but no splashing occurs.

5. Turn the time delay on the Model 633 to 60 s, zero the volume display, then start the titration. When the titration is complete, the meter will be at "EP" and the red light on the Model 655 will turn on.

Calibration

Note: The calibration should be carried out on a daily basis.

1. Attach a B-D No. 5156 needle (22 gauge, 38 mm long) onto a B-D No. 5602 1cc disposable syringe.
2. Put the needle into distilled water, draw the plunger back so that the water comes up to about the 0.05 cc level in the syringe.
3. Remove the needle from the water, draw the plunger back slightly and wipe the needle.
4. Put the syringe on the pan of an analytical balance (one that reads to 0.1 mg), and tare the balance.
5. Insert the syringe through the septum, then eject the contents of the syringe. The meter should immediately point to the far right.
6. Draw the plunger back slightly, then withdraw the syringe from the septum.
7. Place the syringe on the balance pan; the reading will be the negative of the mass of water injected.
8. Check that the volume display is zero, the time delay is 30 s and dV/dt is 2 - 3.
9. Adjust the stirrer speed to have a vortex.
10. Start the titration. When the titration is complete, which should be within 5 minutes, the red light will go on and the meter will point to "EP".

11. Calculate f = mass/volume. Fresh reagent should have a value of about 5. With time, f decreases. A large drop from the previous calibration indicates that either a gross error was made or moisture has entered the system. If f is less than 4, it is advisable to replace the reagent.

Analysis

1. Shake the container of fluid thoroughly to ensure homogeneity.
2. Take a sample of between 0.05 and 0.15 cc in the same way as was done for water.

   Note: A new syringe and needle must be used for each different sample.
3. Weigh out, inject the sample and titrate in the same way as for water.

   Note: The titration time for water/glycols will be less than 5 minutes, for invert emulsions, 30 minutes or more.
4. Calculate the percentage of water in the sample: 100 x volume x f/mass.
5. Repeat twice; if the data are not consistent, repeat several more times.

   Note: The stirrer speed must be increased as the volume of liquid in the vessel increases.
6. Drain the vessel so that the liquid just covers the electrodes. Pour the spent liquid in the plastic drum reserved for that purpose.