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Determination of insolubles in diesel lubricating oil by FIA-visible spectrometry

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Abstract

Insolubles determination is one of the parameters usually recommended to evaluate the residual life of oil because their presence at elevated levels in diesel lubricating oil changes the viscosity, prematurely clogs filters and is one of the major factors in causing abrasive engine wear. The proposed method employs visible spectrophotometric detection in association with flow injection analysis. The results obtained by this method were compared with the ones obtained by Fourier transform infrared spectrometry (FT-IR) since this is the most employed method for insolubles determination. The proposed method presented a linear response from 0 to 3% (w/w) of insolubles in pentane (ASTM D-893). The sampling frequency was about 30 samples h^{-1}, with a relative standard deviation ($n = 5$) of 2.4% or better.

Accuracy was evaluated analysing 98 real samples and the results obtained with the FIA-spectrophotometric method were plotted against those obtained by the FT-IR method by means of linear regression. Slope and intercept of the straight line obtained were compared with the theoretical values of 1 and 0 by means of the joint-confidence ellipse *F*-test. At the confidence level of 95% no evidence of a difference was found between both methods.

Keywords: Insolubles determination; Flow injection analysis (FIA); FT-IR Visible spectrometry

1. Introduction

Used lubricating oil analysis is a widely used tool for predictive and proactive maintenance [1,2].

The traditional property test includes kinematic viscosity, total base number, fuel dilution, wear metals and insolubles. Insolubles include soot, wear metals and oil insoluble resinous matter originating from oil or additive degradation.

Insolubles determination is usually recommended to evaluate the residual life of oil because their presence at elevated levels in diesel lubricating oil changes the viscosity, prematurely clogs filters and is one of the majors factors in causing abrasive engine wear [3,4].

Insolubles determination is based on gravimetric and optical methods. Gravimetric methods include filtration [5], centrifugation [6], and thermo-gravimetric (TGA) [7] procedures.

Filtration and centrifugation techniques are very time consuming (about 2 h each determination) and require the use of large amounts of solvents.

TGA tends to be the standard method of choice and is the only direct measurement of soot as elemental carbon. It is too lengthy to be considered as a routine method and it tends to be a specialist technique and therefore has limited potential beyond the laboratory.

Analysis applying optical methods involves measuring radiation scattering in the infrared and visible region.

Fourier transform infrared spectrometry (FT-IR) provides the most used alternative of all methods. Classically a fixed pathlength cell has been used for the analysis of lubricating oils. In this case, the infrared beam passes directly trough the sample to the detector providing a short pathlength. Manually filling and cleaning of these cells results in low sample throughput. Another sampling method that offers a very quick sample throughput is attenuated total reflectance (ATR). In this technique, the infrared beam is reflected through a crystal of a high refractive index. The sample is placed on the surface of the crystal and the

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infrared beam interacts with the sample on the surface. These leads to a loss on sensitivity that makes this method an unsuitable technique for lubricant condition analysis [8,9]. The most important advantage of FT-IR is that many parameters of interest can be measured (water, glycol, insolubles, fuel, nitration, oxidation, sulfation, anti-wear additives, etc.) [8–12]. Other advantages are faster sample processing than in traditional tests, less operator training and no hazardous chemicals except for the solvent to clean the cell. Besides this, requires only about 3 mL of oil for the analysis.

The main disadvantages are the high cost of the equipment (software included) and the fact that the KBr crystals of the cell are moisture sensitive and can be damaged by abrasive particles which could clog or scratch them. Windows of ZnSe which are insoluble in water overcome part of this problem but are much more expensive.

In this work, measurements with visible spectrophotometry were explored with the purpose of finding a less expensive alternative to FT-IR that could be used in routine analysis in laboratories that have more simple technology without losing precision and accuracy. In order to employ the commonly used cells of 10 mm of optical path great dilutions of the sample are required. Dilutions of such viscous samples are tedious and troublesome.

Flow injection analysis (FIA) has been widely used since its beginning [13] and is a well-known dilution tool. Several flow injection procedures have been developed to promote dilutions exploiting the sample dispersion in the carrier stream. Among its advantages are the feasibility of determinations with minimum manipulation, low cost, easy automation, high sampling rate and a minimum sample and reagent consumption [14].

Spectrophotometry is a widespread detection technique employed in association with flow injection analysis. In order to obtain the required dilution factors a cascade dilution procedure has been reported [15]. Therefore, the aim of the present work was to project a FIA-spectrophotometric method for the determination of insolubles.

2. Experimental

2.1. Samples

The results reported in this paper were obtained from used lubricating oils taken from trucks, buses, cars, ships and locomotives.

2.2. Instrumentation

Measurements of insolubles by FT-IR were carried out using a Nicolet Protege 460 spectrophotometer (Nicolet, Madison, WI, USA) with a 100 μm potassium bromide demountable transmission cell (PIKE Technologies, Madison, WI, USA, model 162–1100).

TQ Analyst version 1.2 was the software used to quantify and OMNIC® to collect the spectra (Nicolet).

Visible spectrophotometric flow injection measurements were carried out in the system schematically shown in Fig. 1. It consists of a six-port injection valve (C22-3186, Valco, Houston, Texas, USA), polytetrafluoroethylene (PTFE) tubing (0.8 and 0.5 mm i.d.), Viton® pump tubing, a eight-channel Gilson Minipuls 2 peristaltic pump (Villiers Le Bel, France), a packed mixing reactor made of 2.48 mm i.d. PTFE tubing filled with small pieces of the same material and PTFE fittings (Omnifit, England) [16].

Detection was carried out with an UV–vis spectrophotometer Shimadzu UV 240 with a graphic printer PR1 module, (Kyoto, Japan) and with an optical glass flow cell (Hellma, Müllheim, Germany, model 178710).

A centrifuge (International Equipment Company, Boston, USA, model BE50) working at a speed of 1600 rpm was used to determine insolubles in pentane by the centrifugation standard method.

A wrist action mechanical shaker was employed to shake samples.

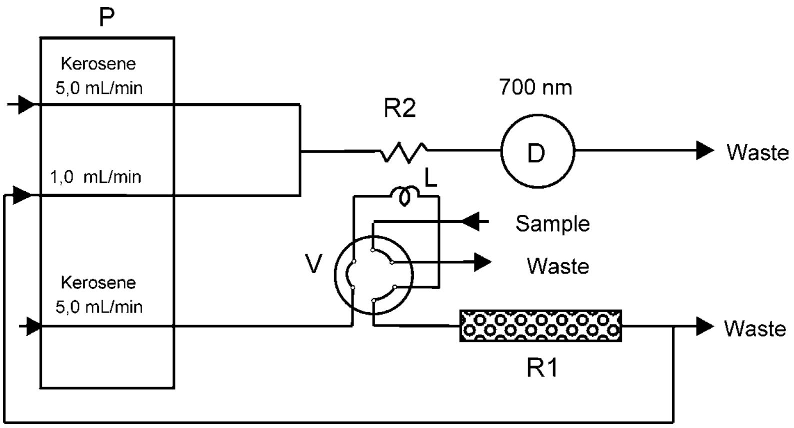

Fig. 1. Flow diagram. P: peristaltic pump; V: injector valve; R_1: packed reactor; R_2: tubular reactor (30 cm); D: detector; L: loop.

2.3. Reagents

Deodorized kerosene (ANCAP, Montevideo, Uruguay) has been used as diluent for the proposed method.

Unused SAE-40 Diesel lubricating oil (Superdiesel 40, ANCAP) was employed as a blank sample and diluent of standards.

Hexane, anhydrous (Dexin, Uruguay) was employed as cleaning solvent for the FT-IR cell.

Pentane 98% (GC Area%) (Sigma, USA) was employed as diluent, *N*-butyl diethanolamine 99% (GC Area%) (Fluka, Germany) and isopropyl alcohol 99.5% (GC Area%) (Sigma, USA) were employed as coagulant for the centrifugation standard method.

2.4. Standard samples for calibration

As there is no available certified standards for insolubles in used lubricating oils it was necessary to determine the amount of insolubles in real samples according with a centrifugation standard method [6].

Insolubles measurements by optical methods and gravimetric methods have not good correlation [8,17]. Insolubles loading causes a shift and tilt in the baseline due to Tyndal scattering, which is related to both the particle concentration and the particle size distribution. Both parameters, particle concentration and particle size distribution depends on the engine and the lubricant used.

Therefore, calibration solutions were prepared with the most loaded sample available diluted with unused oil. The sample used was taken from a locomotive and solutions were prepared by weight. The same solutions were used to create the calibration graphs for both methods. Condemnation limits related to insolubles content for used oils are expressed in percent (%) of insolubles in pentane (w/w). In order to express the results in percent (%) of insolubles in pentane (w/w) calibration solutions were measured by the centrifugation standard method. Calibrations graphs were constructed with five points including the blank (unused oil), the “standardised sample”, and three dilutions thereof with unused oil.

2.5. Procedure

Previous the analysis, used lubricating oil samples were shaken 30 min in a mechanical shaker.

2.5.1. FT-IR method

FT-IR measurements involved manual sampling introduction (2 mL) and cleaning of the cell with 8 mL of hexane between different samples. Three spectra of each sample without dilution were collected between 4000 and 400 cm^{-1}. The instrument was set up as follows: 16 scans; resolution: 4, and gain amplitude: 2.

Insolubles were measured by taking the absorbance intensity at 2000 cm^{-1}, with no baseline correction, and concentrations were calculated by interpolating this value in the calibration plot with first order correction, by means of the TQ Analyst software.

2.5.2. FIA-visible method

In the flow system a syringe is used to load the loop (15 μL) and a manual injection valve is used to insert the samples into the carrier solvent (the carrier flow is shown in Fig. 1).

A volume of 1.5 mL of sample was passed trough the loop between different samples and 0.5 mL between different injections of the same sample. Calibration solutions (blank, 0.49, 0.94, 1.39 and 1.88% (w/w) of insolubles in pentane) were injected in quintuplicate (the calibration graph is shown in Fig. 2). Absorbance was measured at 700 nm. The absorbance value is obtained by the peak height. The instrument algorithm employed is the six-point successive comparison method. The concentration was calculated by interpolating the absorbance value in the calibration plot.

2.6. Effect of experimental variables

The spectra in the visible region of dilutions from 1/100 to 1/1000 (w/v) (oil/solvent) using the same used oil employed in the calibration solutions was collected and the appropriate dilution factor to obtain absorbance values <1 was selected. The wavelength was selected in order to obtain a minimum dispersion of the signal with it (Fig. 3). With this conditions the dilution factor chosen was 1/600 (w/v) and the wavelength was 700 nm.

As the volume of sample injected is related with the solvent consumption its desirable to inject as small volume as possible, thus the volume of the loop used was determined as the minimum length to fit the valve, and the internal diameter was changed from 0.8 to 0.5 mm. These sample volume (15 μL) produced a suitable peak height (absorbance: <1.0) and one reasonable sampling rate.

The first channel carrier flow selected (5.0 mL min^{-1}) was the one optimised for the reactor employed with the purpose of achieve a good mixture [16].

The second flow (5.0 mL min^{-1}) was chosen to obtain absorbance values <1.

2.7. Interferences

Very high water contamination levels can result in an insolubles value that is artificially high by the FT-IR method [8]. For this reason, the presence of water as a contaminant was studied for the FIA-visible spectrophotometric method. A real sample was loaded with distillate water in quantities that ranged from 1 to 10% (w/w). Above 10% (w/w), the presence of water is easily detectable and becomes the main parameter of diagnostic thus the quantity of insolubles losses its interest. The samples with different water content were measured by the FIA-visible spectrophotometric method and the percent recoveries are higher than 95%. (Table 1).

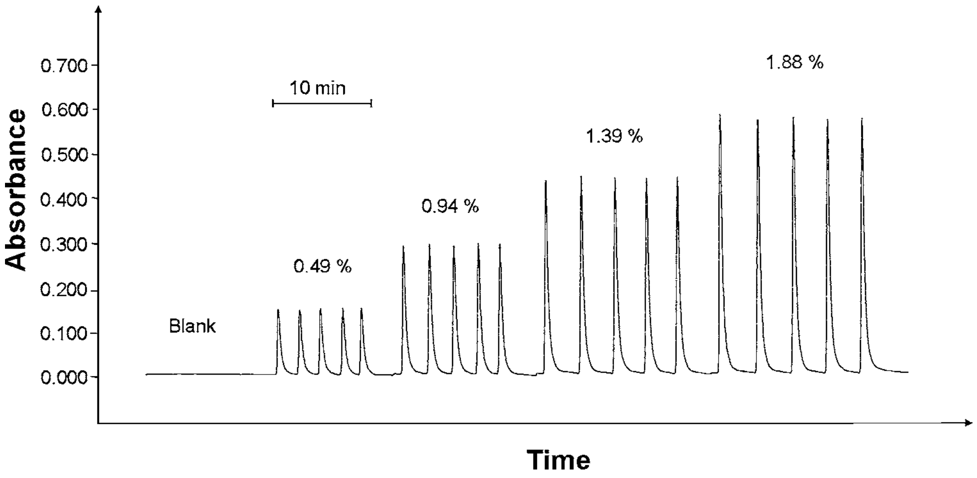

Fig. 2. Recorder output for a calibration curve (0.49, 0.94, 1.39, 1.88% of insolubles in pentane and a blank).

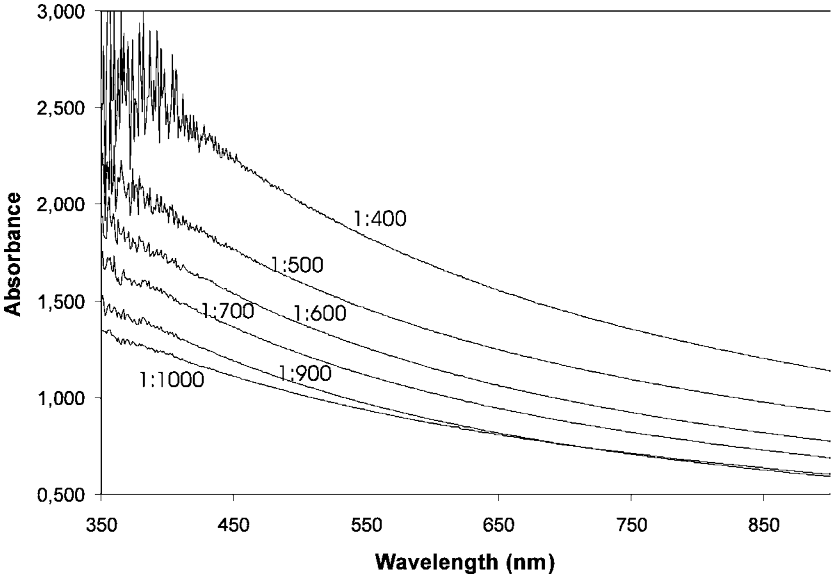

Fig. 3. Recorder visible spectrum for different dilutions factors (oil:solvent) that range from 1:400 to 1:1000 (w/v) of the "standardised" sample (1.88% (w/w) of insolubles in pentane) and kerosene.

2.8. Analytical features of the method

Knowing there was no correlation with the currently available standard methods, the proposed method was compared with FT-IR since this method is the most commonly employed.

Table 1
Effect of water content on insolubles recovery of a sample with 1.04% (w/w) of insolubles in pentane

Water content, % (w/w)	Pentane insolubles, % (w/w)	Recovery (%)
0	1.04	100.0
1.0	1.05	100.6
2.1	1.04	100.0
4.7	1.01	96.8
9.0	0.99	95.2

The proposed FIA-visible spectrophotometric method presented a linear response till 3% (w/w) of insolubles in pentane (ASTM D-893). The sampling frequency was about 30 samples h^{-1}, with a relative standard deviation ($n = 5$) of 2.4% or better. In the FT-IR method the manual filling of the cell and its cleaning is very time consuming so the sampling frequency is minor than in the proposed method.

Accuracy was evaluated analysing 98 real samples and the results obtained with the FIA-spectrophotometric method were plotted against those obtained by the FT-IR method by means of linear regression (Fig. 4). Slope and intercept of the straight line obtained were compared with the theoretical values of 1 and 0 by means of the joint-confidence ellipse F-test (H_0: $a = 1$ and $b = 0$, H_a: $a \neq 1$ and/or $b \neq 0$) [18]. The value of F_{exp} obtained was 2.920 and $F_{0.05}$ (2, 96) = 3.106, so at the confidence level of 95%

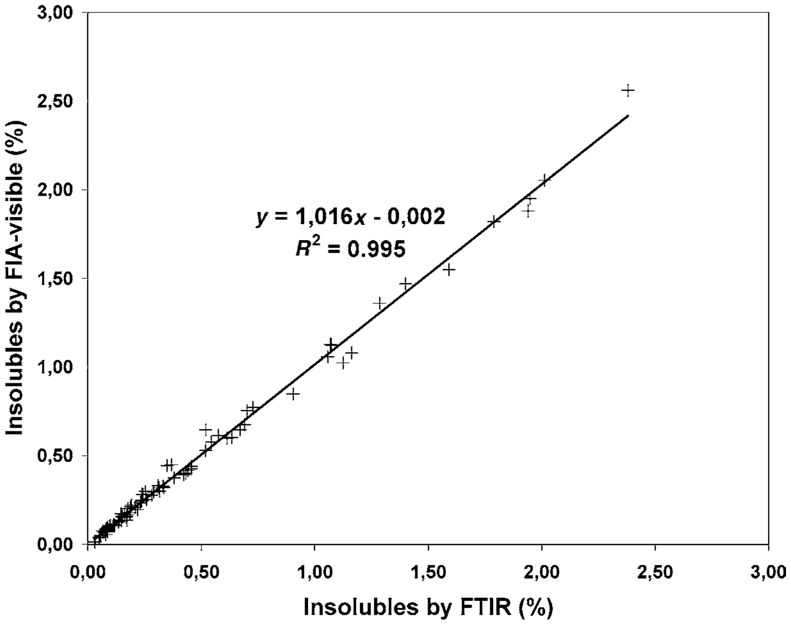

Fig. 4. Correlation of analytical results for insolubles determination by IR and by the proposed FIA-visible spectrophotometric method.

no evidence of a difference between both methods was found.

The proposed method has very simple instrument manipulation and it only requires a pump, an injector and a visible spectrophotometer, which is available in most laboratories. Compared with FT-IR in terms of simplicity, the sampling is easier in the proposed method, while the others steps of the analysis are as simple as in FT-IR.

3. Conclusions

The results suggest that the proposed method can be useful for the determination of insoluble matter in lubricating oils. Among its advantages are less solvent consumption and a considerable analysis time reduction than in the standard methods. Other advantages are the feasibility of achieve large dilution factors faster and easily than in batch procedures and it also requires less expensive instrumentation.

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