

## A RAPID METHOD FOR THE QUANTITATIVE DETERMINATION OF HALOGEN IN USED OILS

Deborah Minucci, Quality Control Manager, Stephen Finch, Laboratory Manager, DEXSIL CORPORATION, One Hamden Park Drive, Hamden, Connecticut 06517

### INTRODUCTION

EPA regulation 40 CFR 261 bars the sale of used oil for fuel if it is contaminated with halogens measured as chlorine at levels exceeding 1000 ppm. Such oil is considered to be a hazardous waste unless it can be proven that the chlorine content is inorganic or that the halogenated organics are not hazardous constituents. The cost of disposing of a hazardous waste is many times higher than the cost of used oil disposal. Therefore, it is critical for users, generators, haulers, reprocessors, and collectors to test the material they handle in order to comply with regulations, maintain safe operations, and avoid high disposal costs. The analytical burden on these various types of companies becomes very significant and costly.

The EPA contracted for an evaluation of analytical technology in order to recommend acceptable methodology. Neutron activation analysis, micro-coulometric titration and X-ray fluorescence were found to be acceptable instrumental approaches, while the LECO chlorine determinator and the Beilstein test device were found to need more development. All of these instrumental approaches require a significant capital investment, trained personnel, and a sample load greater than 10,000 / year to justify the investment.

While some instrumental approaches permit the direct determination of total chlorine in petroleum products, most laboratory methods need to convert organic chloride to inorganic chloride using the ASTM D-808-63 oxygen bomb method as a prerequisite for analysis. The "bomb method" requires a capital purchase of equipment, is time consuming (about 45 minutes per sample), and is highly technique oriented. The chemical approaches evaluated were the finishing ASTM methods following the bombing prerequisite. These methods included ion

chromatography, turbidimetric, mercuric nitrate, silver nitrate, ferricyanide, potentiometric and amperometric methods. All of these approaches worked if the ASTM methods were modified in some way, such as filtering, drying, extracting or various other pre-treatments. The major problem with all of the chemical approaches is the requirement of ASTM – D – 808 – 63, the use of the oxygen bomb.

### KIT DEVELOPMENT

A method has been developed that replaces the lengthy oxygen bomb prerequisite for analysis. This method involves a chemical removal of chlorine, rather than a combustion oxidation removal. Analysis time is approximately ten minutes and the necessary reagents are all contained in a small test kit. Each kit contains sufficient materials for ten analyses.

The materials required for one analysis are two plastic tubes containing predisposed, encapsulated reagents, a filter assembly, and standardized silver nitrate titrant.

Approximately 0.35 grams of sample is weighed into the first tube using an analytical balance. After the tube is recapped, the bottom glass ampule is broken and the tube is shaken for ten seconds. This ampule contains 1.5 mL of a solution containing aliphatic solvent, naphthalene and diglyme, which conditions the waste oil for the analysis. The second ampule is then broken and the tube is shaken for ten seconds, and allowed to react for one minute, shaking intermittently. This ampule contains a dispersion of metallic sodium in an organic matrix that strips the organic chloride from the sample.

The second tube contains seven mL of aqueous buffer solution. After the sodium reaction has been allowed to run for one minute, the buffer solution is

poured from the second tube into the first one which contains the sodium, aliphatic solvent, and oil sample. After a few seconds of shaking, the sodium reaction is quenched and any halogens that are present (now in the ionic form) are extracted into the aqueous solution. The tube is then inverted and allowed to settle for two minutes while the organic and aqueous phases separate. At this point, the dispenser cap on the tube is opened and the buffer solution is through the filter assembly into the second tube. Five mL of the aqueous phase is then pipetted from the second tube into a titration beaker and approximately 40 mL distilled water is added. An automatic or manual potentiometric titration can now take place using a Ag/AgCl electrode.

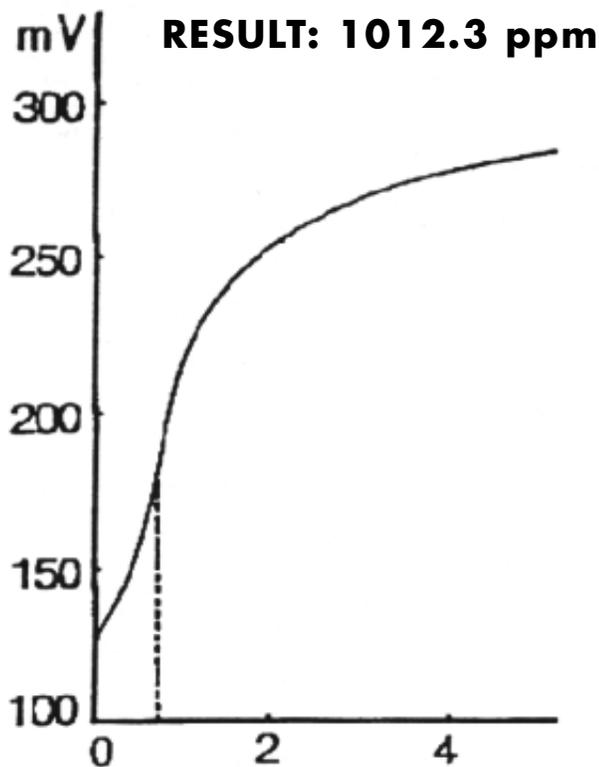


FIGURE 1  
D-113

**Figure 1** illustrates a typical titration curve plotted by the Mettler DL20 automatic titrator equipped

with a DM141 electrode and 5 mL dispensing burette. The sample tested consisted of 1000 ppm trichlorobenzene in used lube oil. This method typically gives a 100 mV spread at the point of inflection.

Table 1		
Sample Type	Cl <sup>-</sup> added (ppm)	Cl <sup>-</sup> found (ppm)
Used Lube Oil	1100	1184
	832	841
Virgin Lube Oil	970	923
	40	44
#6 Fuel Oil	1000	1035

**Table 1** lists some typical results obtained on various types of petroleum products. The results are very acceptable and precision is  $\pm 7\%$ .

This method has been evaluated on virgin lube oil, virgin hydraulic oil, used lube oil, fuel oils #2 – #6, kerosene and transformer oils. The samples must, however, contain less than thirty percent water. If the samples contain greater than thirty percent water, the sodium reacts preferentially with the water rather than with the halogenated organics in the oil.

This method detects iodine, bromine and chlorine equally. It does not detect fluorine because AgF stays in solution during the titration, while AgI, AgBr, and AgCl precipitate out and can therefore be detected.

Fluorine does not interfere with the detection of the other halogens present. **Table 2** lists recovery of other halogen types in a #6 fuel oil and recovery of halogen from a mixed halogen in used lube oil.

<b>Table 2</b>		
<b>Material Added</b>	<b>Cl<sup>-</sup> Added (ppm)</b>	<b>Cl<sup>-</sup> Found (ppm)</b>
Bromobenzene	1100	1151
Iodobenzene	1100	1033
Fluorobenzene	1100	15.9
Trichloro-	832 (added as Cl <sup>-</sup> )	841
trifluoroethane	446 (added as F <sup>-</sup> )	0

**Table 3** lists some chlorinated organic compounds which have been shown to be detectable by the potentiometric titration.

<b>Table 3</b>
Trichloroethane
Dichloroethane
Trichlorobenzene
Monochlorobenzene
Chlorooctadecane
Methylene Chloride
Perchloroethylene
Freon (113)
Polychlorinated Biphenyls

By verifying that the kit works on these nine compounds we have covered the major classes of chlorinated compounds that we expect to find in used oils. Volatile degreasing solvents (1,1,1 trichloroethane) are expected to be densely chlorinated aliphatics, cleaning solvents, refrigerants, and PCBs.

This method is now available from Dexsil in kit form. Complete, each kit contains sufficient materials for ten analysis. The cost is \$60 per kit, or \$6 per analysis. Total cost per analysis is significantly reduced by the four fold (400%) reduction in analysis time over conventional methods.