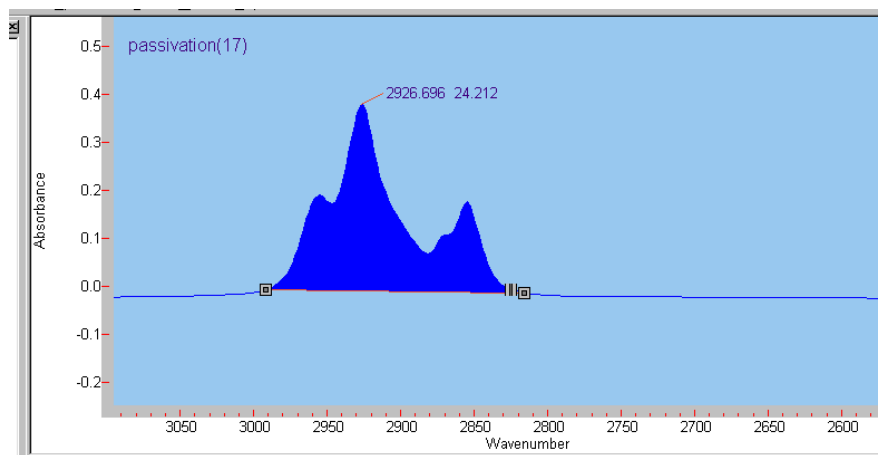


Introduction

Porous titanium coatings are often used in orthopedic prosthesis due to their efficacy in inducing bone growth into the porous coating. This in-growth generally provides good fixation of the implant. It has been recently observed that excessive amounts of mineral oil were found in a series of porous titanium-backed acetabular shells. This mineral oil was introduced during the machining process as a cutting fluid, and was not removed during the cleaning process. A technique was needed to quantify the amount of oil that could be extracted from these components, in order to assess the dependence of bone in-growth on oil content. This application note outlines the extraction and analysis protocol designed for this task, and describes validation tests performed to determine the sensitivity and accuracy.

Extraction and Analysis Technique

The main objective was to find an extraction technique that would remove all trace amounts of mineral oil from the porous titanium shell, then allow quantification of the amount of oil in the extract. The amount of oil in the shells was suspected to be in the milligram range, so a technique sensitive enough to measure ppm quantities was necessary. Infra-red spectroscopy was identified as a possible technique. Mineral oil is a short-chain hydrocarbon, and thus only exhibits absorption peaks associated with C-H rocking, stretching, and bending. Most conventional solvents for mineral oil also contain C-H bonds, and would thus overwhelm the absorption peaks arriving from the mineral oil alone. Thus, halogenated solvents were examined. Carbon tetrachloride was selected as an obvious choice. It is a good solvent for mineral oil and, lacking any C-H bonds, will not exhibit an absorption peak around 2900 cm^{-1} where the mineral oil has a strong series of peaks, as shown below:



Absorption spectra for mineral oil.

The extraction protocol required extremely clean glassware, IR sample cells, and component handling equipment. All equipment that would come in contact with the orthopedic components were ultrasonicated in chloroform to remove all trace hydrocarbons, then carefully dried.

**Mineral Oil Extraction from
Porous Titanium Surfaces**

The orthopedic shell was placed in a pre-weighed extraction vessel, which was filled with approximately 100 ml of spectroscopy grade carbon tetrachloride (>99.9%). The vessel was covered, then sonicated for 1 hr. After sonication, the shell was removed with clean forceps, rinsed back into the vessel with carbon tetrachloride, then dried. The extraction solution was then concentrated by evaporating some of the carbon tetrachloride by heating. The vessel with solution was weighed prior to infra-red analysis, in order to determine the solution weight.

Calibration System for Mineral Oil Extraction

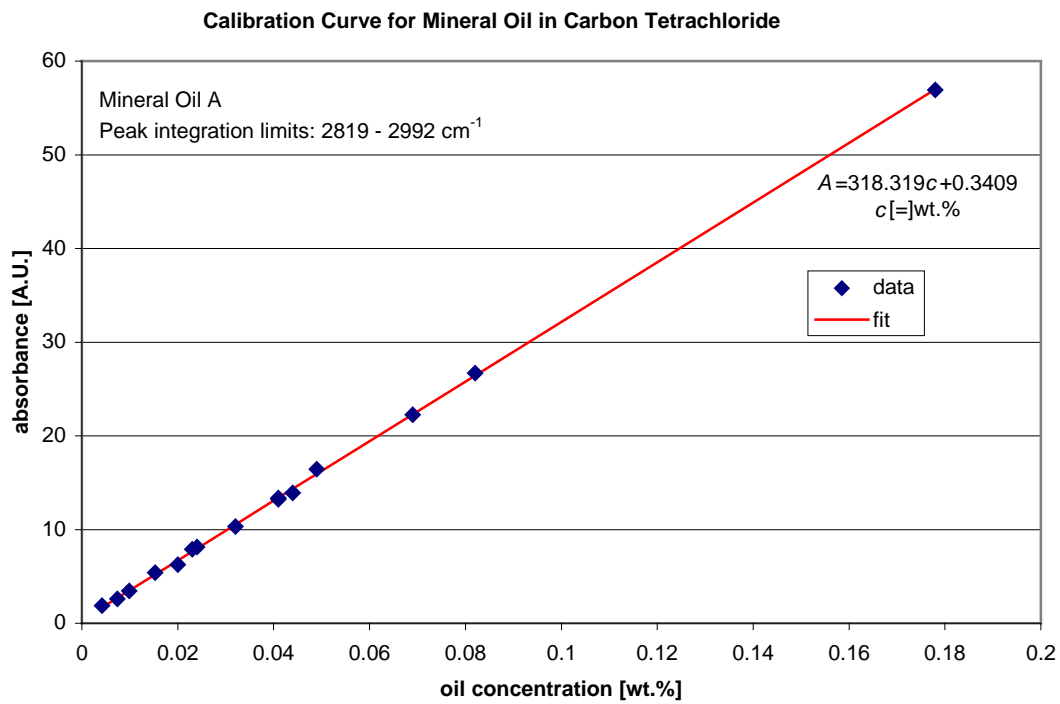
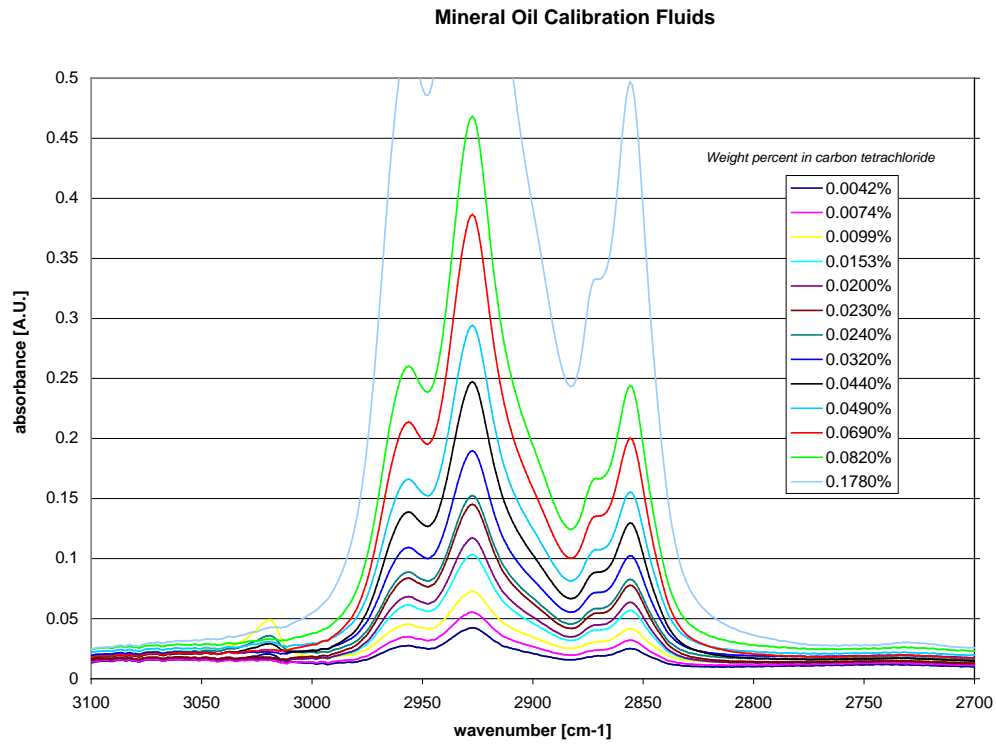
In order to quantify the amount of oil in the solution, a calibration curve had to be constructed. To do this, a series of calibration solutions containing trace amounts of mineral oil (0.8 mg to 30 mg) and carbon tetrachloride were prepared to generate a master curve for FTIR analysis. The raw spectra, focusing on the peaks specific to mineral oil, are shown in the plot below. The area under the peaks associated with the mineral oil was integrated from 2819 to 2992 cm^{-1} and plotted as a function of the oil concentration yielding the calibration curve shown below. Preliminary extraction results show a mineral oil sensitivity of 0.02 mg oil in an extraction volume of 12 ml.

The calibration curve shows the linearity of Beer's Law, which states that the absorption A of a sample is a function of the concentration c of the absorbing component, the path length b , and the absorptivity of the component ϵ according to:

$$A = \epsilon bc$$

From the plot shown below, the slope is proportional to the product ϵb , yielding an absorptivity of $\epsilon=318 \text{ mm}^{-1}$ (the path length was 1 mm).

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The oil concentration c in the test solution is determined from the calibration curve after measuring the absorbance area. The mass of oil extracted from the component m_{oil} is determined from the mass of solution $m_{solution}$ as

$$M_{oil} = cm_{solution}$$

Test Samples

The efficacy of the technique was determined with test samples that contained a known quantity of mineral oil, as measured with a microbalance. Extraction was performed with carbon tetrachloride as outlined above. The samples were stored in cellulose-based envelopes temporarily, which wicked out some of the oil in the more heavily doped samples.

The table below shows the results. The maximum difference was 0.6 mg, which is almost within the expected error of the microbalance used to weigh the oil (0.2 mg resolution * 2 measurements = 0.4 mg error).

Test Sample Analysis

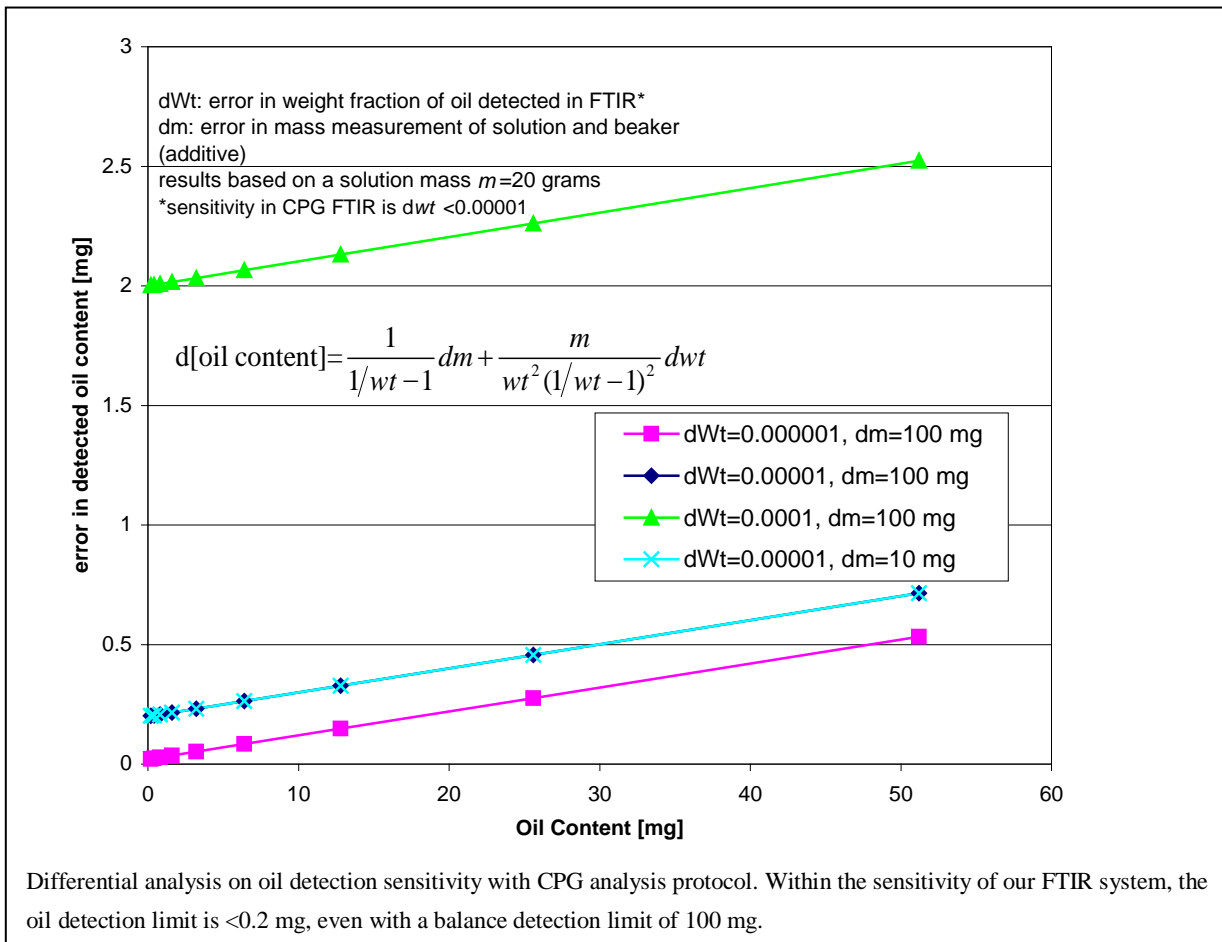
Sample	Measured Oil Content** [mg]	Applied Oil Content [mg]	Difference [mg]
1	0.02	0	0.02
2	0.20	0	-0.2
3	2.01	1.78	-0.24
4	2.55	2.62	-0.07
5	9.95	10.06	-0.11
6	10.49	10.35	-0.14
7	20.01	19.83	0.18
8	29.44	29.91*	-0.47
9	29.54	30.16	0.62
10	41.00	41.54*	-0.54

**determined via CCl₄ Extraction/IR technique

*residual oil observed on sample envelope

Differential Sensitivity Analysis

The sensitivity of the residual oil measurement on the resolution of the weight measurement and infra-red measurement was determined from a simple differential sensitivity analysis on the equation used to calculate the oil content. The dependence is shown below, and indicates that the oil detection limit is below 0.2 mg, even with a balance resolution of 100 mg. This apparent discrepancy is due to the high sensitivity of the infra-red detection technique, which allows measurements of extremely small concentrations of mineral oil.



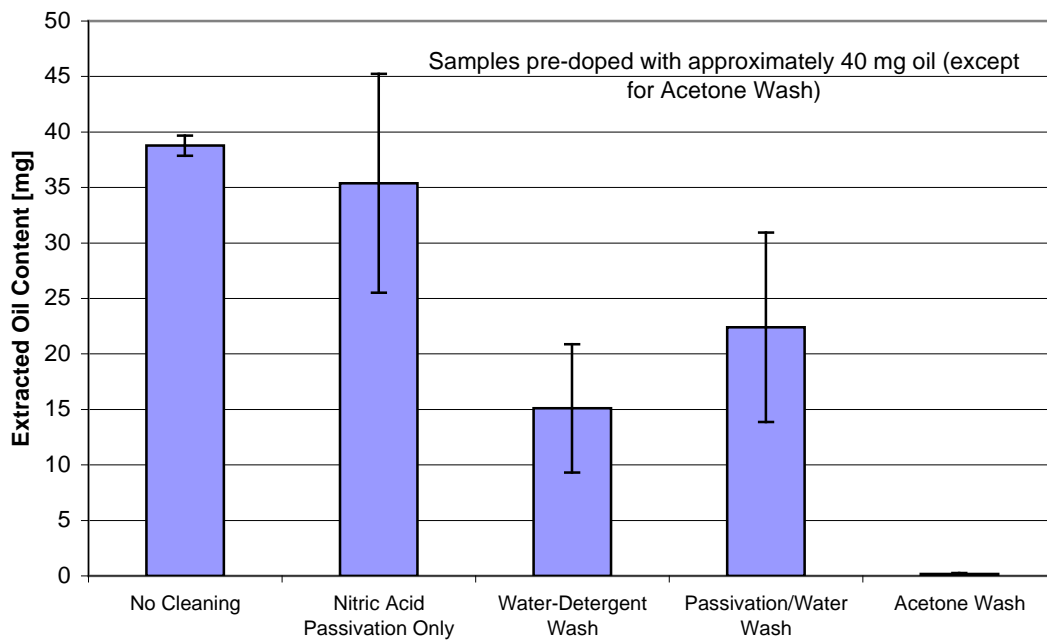
Dependence of Mineral Oil Content on Cleaning Procedure

Five series of shells were examined to assess the efficacy of the various steps used in cleaning orthopedic components. Porous titanium backed acetabular shells were pre-doped with approximately 40 mg of mineral oil, the subjected to one or more of the following cleaning processes:

1. Control: no further cleaning was performed
2. Nitric acid passivation: samples were passivated in 35% nitric acid solution
3. Water wash: samples were washed in a commercial detergent/water cleaning system
4. Acetone wash: the samples were sonicated in acetone.

A minimum of 9 specimens were examined for each process, and as many as 120 were examined for the acetone washing process. The results shown below indicate that nitric acid passivation does not remove measurable amounts of oil, while the water-wash system removes approximately half of the dopes oil. The acetone wash specimens had residual oil levels below 0.2 mg.

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Mineral Oil Extraction from
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Dependence of residual oil content on washing protocol for porous titanium-backed acetabular shells.

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