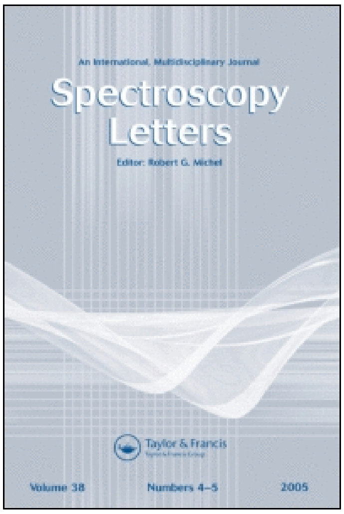

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

A Rapid Method for the Determination of Trace Element Impurities in Silicons Oils by ICP-MS After Microwave-Assisted Digestion

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To cite this Article Das, Arabinda K. , Chakarborty, Ruma , Cervera, M. Luisa and de la Guardia, Miguel(1998) 'A Rapid Method for the Determination of Trace Element Impurities in Silicons Oils by ICP-MS After Microwave-Assisted Digestion', Spectroscopy Letters, 31: 6, 1245 — 1253

To link to this Article: DOI: 10.1080/00387019808003299

URL: http://dx.doi.org/10.1080/00387019808003299

SPECTROSCOPY LETTERS, 31(6), 1245-1253 (1998)

A RAPID METHOD FOR THE DETERMINATION OF TRACE ELEMENT IMPURITIES IN SILICONE OILS BY ICP-MS AFTER MICROWAVE-ASSISTED DIGESTION

Keywords: Silicone oils, trace elements, ICP-MS, microwave-assisted digestion.

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ABSTRACT

A microwave-assisted digestion procedure has been developed for the treatment of silicone oil samples. Inductively coupled plasma mass spectrometry (ICP-MS) was used to determine the concentration level of 40 trace element impurities, like Li, Na, Mg, Al, P, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Sr, Rb, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Ba, La, Ce, Nd, Hf, W, Au, Pb, Hg, Th, Bi and U in these samples, having obtained average relative standard deviation values of 9.6%. The methodology developed has been tested by recovery studies on different natural samples spiked with known amounts of Mg, Cr, Mn, Fe, Zn and Pb at concentration levels of 10, 0.5, 5, 5, 10 and 1 μg g^{-1} and recovery percentage values varies from 97 to 105 %.

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INTRODUCTION

Silicone fluids, commonly called silicone oils, are linear organosilicon polymers with a common chain made of repetitive siloxane units. These compounds have been used for many years in food, pharmaceutical, health and beauty products, adhesives, sealants, and many other commercial products[1], the silicone oils being also employed to retinal surgery from the year 1962[2].

Although produced synthetically, all silicone oils contain a certain amount of catalytic and processing by-product impurities and also, transferring the polymer from manufacturing vessels to selling containers also can increase the number and quantity of impurities.

It has been reported, although not verified, that catalysts and impurities produce intraocular tissue reaction[3] and, because of that it is very important to measure and control the impurity concentrations of various elements present in silicone oil.

On the other hand, the analysis of silicone oils is a challenging analytical problem[4] owing to various factors, like the ease interaction of silicones with container walls, the high probability of external contamination and finally its behaviour in front of inorganic acids. Hence the work on silicone matrix is scarce, having found only one paper in which it has been reported the determination of various elements by inductively coupled plasma optical emission spectroscopy in a silicone matrix[5].

The search for simpler, more reliable and less expensive methods for sample dissolution continues to be a major goal to be achieved in atomic spectrometry. In this sense microwave-assisted digestion appears to be a very attractive aid for sample dissolution specially because it is very fast and can be applied to the treatment of any type of samples[6-8].

High-pressure microwave digestion for the determination of As, Sb, Se and Hg in oily waters was described by Campbell and Kanert[9], but we do not have found precedents about the use of microwave-assisted procedures for the digestion of silicone oil samples.

Inductively coupled plasma mass spectrometry (ICP-MS) is now-a-days accepted as a fast, reliable and very sensitive technique for multielemental analysis of a wide variety of sample types[10,11], and because of that the aim of this study is the development of an analytical method for the determination of trace impurities in silicone oil samples after sample dissolution by means a microwave-assisted treatment.

EXPERIMENTAL

Apparatus, Reagents and Samples

An Inductively Coupled Plasma Mass Spectrometer SCIEX Elan 5000 from Perkin Elmer Sciex (Thornihill, Ontario, Canada) was employed in the present study and yttrium was used as internal standard. The typical instrumental operating and measurement conditions are given in Table 1.

A domestic Moulinex Super Crousty microwave oven (Paris, France) with 2450 MHz frequency magnetron and 1100W maximum power and homemade polytetrafluoroethylene (PTFE) reactors with 115 cm^3 internal volume, 1 cm wall thickness and hermetic screw caps, were used for the digestion of silicone oil samples.

All reagents used were of the highest purity available and at least of analytical reagent grade. HNO_3 69%, d=1.42 g cm^{-3} from Merck (Darmstadt, Germany), HCl 37%, d=1.18 g cm^{-3} from Fluka (Buchs, Switzerland), HF 48%, d=1.14 g cm^{-3} from Panreac (Barcelona, Spain) and H_2O_2 33% 110 volumes from Scharlau (Barcelona, Spain) were employed for sample treatment. High purity water was obtained with a Barnstead Nanopure II water-purification system (MA, USA) with a resistivity of 18 MΩcm.

All glassware were soaked in 10% (v/v) nitric acid for 24h and washed with deionized water prior to use.

Five silicone oil samples were employed in the present work; of which one is a commercially available product from Probus (Barcelona, Spain) (sample 1) and the other four were produced for retinal surgery at different purity levels (samples 2, 3, 4 and 5 correspond to 100CS pure silicone, 100CS unpurified silicone, 1000CS pure silicone and 1000CS unpurified silicone, respectively).

Microwave-Assisted Digestion Procedure

Microwave oven-assisted digestion procedures for the treatment of environmental, biological and geological materials have been described earlier in detail by our research group[12-13]. In the present study, this methodology has been applied, increasing the number of steps and the amount of HF, in order to ensure the complete dissolution of silicone oil samples and the quantitative extraction of trace element impurities in the shorter as possible period of time.

TABLE 1

Instrumental operating conditions by ICP-MS

Plasma Argon flow	15.0 $dm^3\ min^{-1}$
Nebulizer Argon flow	0.9 $dm^3\ min^{-1}$
Auxiliary Argon flow	0.8 $dm^3\ min^{-1}$
Rf Power	1000 W
CEM voltage	3200 V
Sample uptake	1.0 $cm^3\ min^{-1}$

General Procedure

A mass of 70 to 150 mg of silicone oil sample was accurately weighed and treated sequentially with 5 cm^3 aqua regia, 5 cm^3 HF and 2 cm^3 H_2O_2 in an hermetically sealed PTFE reactor inside a microwave oven using digestion steps of 5 minutes at 220W after the addition of each one of these reagents and additional two steps of 5 minutes at 440W and 3 minutes at 550W in order to obtain a clear solution. Then solutions were treated with 12.5 cm^3 of a saturated H_3BO_3 solution in a hot waterbath for 10 minutes and diluted to 50 cm^3 with distilled water.

Real samples and spiked ones were treated and analysed by ICP-MS in triplicate and three acid blank solutions were measured following the aforementioned procedure.

RESULTS AND DISCUSSION

Rapid Microwave-Assisted Digestion of Silicone Oils

A combination of aqua regia, HF and H_2O_2 was employed in order to achieve an efficient and rapid digestion of the silicone oil samples.

The main objective was to obtain the total dissolution of samples or at least to obtain the maximum extraction of trace components into the acid phase, in the shortest time in order to increase the laboratory productivity and using the minimum amount of acids to avoid molecular interferences in the ICP-MS. As the amount of acids required for the digestion depends on the quantity of sample treated, the sample size was restricted to less than 200 mg.

Further tests were carried out to select the minimum amount of acids required for treatment of less than 200 mg of sample and to decide the final volume of the sample solutions. Samples of 100 mg were treated with 5 cm^3 aqua regia, followed by an additional treatment with 5 cm^3 HF and that with 2 cm^3 of 33% (m/v) H_2O_2 in order to totally dissolve the samples without introducing a big amount of acids.

In order to avoid leaks during the pressurized acid sample treatment the power was drastically reduced during the first treatment steps and its duration fixed in 5 minutes.

Through the present study, 5 cm^3 of aqua regia were added to samples and after a 5 min irradiation at 220W the reactor was cooled and 5 cm^3 HF added, carrying out the second step of digestion for 5 min also with a power of 220W. The complete dissolution of the remaining residue was carried out by treating with 2 cm^3 of a 33% (m/v) H_2O_2 solution for 5 min at a power level of 220W again. Additional digestion steps were also performed at a power of 440W for 5 min then at 550W for 3 min thus providing a total irradiation time of 23 minutes. An additional treatment with 12.5 cm^3 of a saturated H_3BO_3 solution for 10 min, in a boiling waterbath, was included to provide destruction of the excess HF.

In the aforementioned conditions samples were totally dissolved without providing any solid residue. Blank assays were also carried out on the same conditions than sample digestion having confirmed that the acid treatment provides very low background levels thus improving the detection of ultratrace amounts of impurities.

Analytical Performance

Detailed results of the analysis of silicone oil samples and the precision of such measurements, expressed as the standard deviation of three independent analysis are given in Table 2. Sample S1, a commercially available silicone oil reagent, contains lower concentrations of elemental impurities than the other samples assayed. Nevertheless, these latter four samples (S2 to S5) contain the impurities in more or less similar amounts, and it is clear that the purification process applied to treat samples S3 and S5 can reduce the content of some of the elements under study. From data in Table 2 it can be seen that the average relative standard deviation is 9.6%.

TABLE 2

ICP-MS determination of impurities in silicone oil samples after microwave-assisted digestion

Element	Silicone oils / element concentration in $\mu g\ g^{-1}$				
	S1	S2	S3	S4	S5
Li	0.34 ± 0.05	0.8 ± 0.1	1.4 ± 0.1	1.05 ± 0.05	1.31 ± 0.08
Na	290 ± 30	1500 ± 200	1700 ± 200	1600 ± 200	1700 ± 200
Mg	42 ± 5	41 ± 4	69 ± 6	41 ± 4	56 ± 5
Al	840 ± 90	1300 ± 100	1400 ± 100	1170 ± 90	1300 ± 100
P	91 ± 7	120 ± 10	139 ± 9	104 ± 8	141 ± 8
Ca	1800 ± 200	2100 ± 200	2500 ± 100	2400 ± 100	2500 ± 100
Sc	1.8 ± 0.1	18 ± 2	25 ± 2	18 ± 2	25 ± 2
Ti	9.0 ± 0.7	710 ± 60	930 ± 80	740 ± 60	1100 ± 100
V	0.02 ± 0.01	3.6 ± 0.3	4.6 ± 0.4	2.9 ± 0.2	3.6 ± 0.3
Cr	1.1 ± 0.1	5.6 ± 0.4	5.7 ± 0.5	6.4 ± 0.5	8.9 ± 0.7
Mn	31 ± 4	33 ± 3	34 ± 3	27 ± 2	30 ± 2
Fe	29 ± 3	92 ± 4	106 ± 9	94 ± 6	97 ± 6
Co	0.24 ± 0.03	0.40 ± 0.03	0.77 ± 0.08	0.35 ± 0.02	0.48 ± 0.03
Ni	0.57 ± 0.07	0.98 ± 0.05	1.1 ± 0.2	0.50 ± 0.02	0.57 ± 0.03
Cu	0.62 ± 0.07	0.96 ± 0.05	1.7 ± 0.2	3.3 ± 0.3	3.74 ± 0.03
Zn	270 ± 30	130 ± 10	160 ± 10	260 ± 30	260 ± 30
Ga	0.23 ± 0.03	1.21 ± 0.08	2.3 ± 0.2	1.23 ± 0.09	2.6 ± 0.3
As	140 ± 10	150 ± 10	190 ± 10	160 ± 10	160 ± 10
Se	0.64 ± 0.07	3.2 ± 0.3	12 ± 1	10 ± 1	18 ± 2
Sr	6.8 ± 0.8	13 ± 2	40 ± 4	12 ± 2	33 ± 4
Rb	0.04 ± 0.01	1.3 ± 0.1	3.7 ± 0.3	2.8 ± 0.2	3.1 ± 0.2
Zr	24 ± 2	118 ± 9	129 ± 9	102 ± 5	120 ± 9
Nb	0.09 ± 0.02	0.57 ± 0.04	0.67 ± 0.08	0.45 ± 0.03	0.66 ± 0.03
Mo	0.24 ± 0.02	2.1 ± 0.2	2.7 ± 0.2	1.7 ± 0.1	2.1 ± 0.2
Ag	0.09 ± 0.02	0.27 ± 0.03	0.38 ± 0.03	0.17 ± 0.02	0.19 ± 0.03

TABLE 2. Continued

Element	Silicone oils / element concentration in μg g^{-1}				
	S1	**S2**	**S3**	**S4**	**S5**
Cd	0.09 ± 0.02	0.15 ± 0.02	0.20 ± 0.03	0.06 ± 0.01	0.14 ± 0.02
Sn	0.07 ± 0.01	22 ± 2	28 ± 2	24 ± 2	34 ± 3
Sb	33 ± 4	42 ± 4	54 ± 4	39 ± 3	46 ± 4
Ba	90 ± 9	430 ± 40	600 ± 60	360 ± 30	690 ± 50
La	0.11 ± 0.02	2.0 ± 0.2	3.7 ± 0.3	2.4 ± 0.2	3.3 ± 0.2
Ce	0.88 ± 0.07	4.8 ± 0.3	9.0 ± 0.6	4.6 ± 0.4	5.9 ± 0.4
Nd	0.10 ± 0.02	2.1 ± 0.2	3.8 ± 0.3	2.4 ± 0.2	2.9 ± 0.3
Hf	0.87 ± 0.06	4.8 ± 0.4	6.1 ± 0.5	4.6 ± 0.4	5.7 ± 0.5
W	0.14 ± 0.01	0.51 ± 0.07	0.8 ± 0.1	0.42 ± 0.04	0.53 ± 0.05
Au	0.01 ± 0.00	0.14 ± 0.02	0.16 ± 0.02	0.02 ± 0.00	0.02 ± 0.00
Pb	3.2 ± 0.1	6.9 ± 0.4	27 ± 1	9.5 ± 0.7	20 ± 2
Hg	0.21 ± 0.02	0.43 ± 0.03	0.60 ± 0.04	0.62 ± 0.03	0.72 ± 0.04
Th	0.04 ± 0.01	1.18 ± 0.08	1.53 ± 0.09	0.19 ± 0.02	0.86 ± 0.04
Bi	0.09 ± 0.01	0.11 ± 0.02	0.14 ± 0.02	0.12 ± 0.02	0.18 ± 0.03
U	0.12 ± 0.02	0.73 ± 0.05	1.20 ± 0.05	0.76 ± 0.04	0.96 ± 0.05

S1 = silicone oil (Probus, Spain); **S2** = 100CS pure silicone oil; **S3** = 100CS unpurified silicone oil; **S4** = 1000CS pure silicone oil; **S5** = 1000CS unpurified silicone oil; mean value ± standard deviation for n = 3

To evaluate the accuracy of the method, recovery studies were carried out by spiking real samples with known amounts of various elements and using the proposed general procedure. Table 3 shows the obtained recoveries for the following test elements: Mg, Cr, Mn, Fe, Zn and Pb, at spiked concentration levels of 10, 0.5, 5, 5, 10 and 1 μg g^{-1} respectively, with their relative standard deviation. From these data it can be seen that quantitative recoveries can be achieved in the aforementioned conditions, thus indicating that the sample treatment does not provides element losses nor contaminations thus being useful for the analytical control of trace elements in silicone oils.

TABLE 3

Analytical recovery values for six test elements added to the different silicone oil samples assayed

Sample	Element Recovery (%)					
	Mg	Cr	Mn	Fe	Zn	Pb
S1	97 ± 4	104 ± 2	105 ± 1	97 ± 4	99 ± 3	101 ± 4
S2	99 ± 3	103 ± 2	102 ± 4	97 ± 2	99 ± 4	105 ± 2
S3	99 ± 3	102 ± 1	104 ± 4	98 ± 3	100 ± 2	103 ± 2
S4	98 ± 4	103 ± 3	104 ± 1	99 ± 4	99 ± 4	102 ± 2
S5	98 ± 3	104 ± 3	102 ± 1	99 ± 3	100 ± 3	102 ± 2

Percentage of recovery and relative standard deviation for n = 3. Spiked levels for Mg, Cr, Mn, Fe, Zn and Pb are respectively 10, 0.5, 5, 5, 10 and 1 $\mu g\ g^{-1}$.

From the studies carried out it can be concluded that silicone oil samples can be digested successfully using the proposed microwave-assisted treatment in a total time of less than 30 minutes. This sample preparation procedure not only significantly shortens the time required for sample dissolution but also employs less acid amount thus providing less risks of contamination and a more environmentally friendly analytical methodology than those based on classical digestion procedures. As the samples have been analysed by ICP-MS, the total time required for all the sample components analysis is further reduced.

POTENTIAL HAZARD WARNING

Through this study, a domestic microwave oven, without any modification was employed and thus it does not requires additional warning as it is absolutely necessary when the ovens are modified in order to introducing cooling systems or provide fume escapes. On the other hand, the use of hermetically closed teflon reactors avoids acid or sample leaks and fume escapes, thus providing a safe and clean way to do the sample digestion having not found any problem on the use of the recommended procedure during the development of this study.

ACKNOWLEDGEMENTS

Two of the authors (RC and AKD) thank the Universitat de Valencia (Spain) for providing the facilities to carry out the present work. The financial support of the Conselleria de Cultura, Educació i Ciència de la Generalitat Valenciana, Project no. GV-2232/94 is also acknowledged.

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Date Received: March 30, 1998
Date Accepted: May 8, 1998