

Saponification Values of Waxes by Microwave Instead of Conventional Heating

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Abstract:

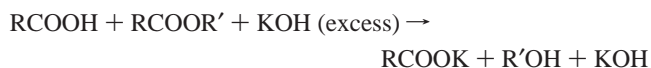
A method is described for the determination of the saponification values of waxes using microwaves in place of conventional heating. Statistical analysis shows that the new method gives the same results as the conventional method in spite of a dramatically shortened analysis time.

Introduction

Waxes have been known to mankind for several thousands of years and are today a widely used chemical commodity throughout the world (ca. 800 000 tonnes marketed per annum) due to certain intrinsic and valuable properties.^{1,2} They are used, for example, in candles, polishes, hot-melt adhesives, lubricants, electrical insulation, paper coatings, inks, cosmetics, pharmaceuticals, textile processing, and food-related applications—including chewing gum. Different sources tend to define waxes differently, but it is generally agreed that they are hydrocarbon-based materials and solid at room temperature. They are usually classified according to their origin: they can be derived from *natural* sources (animal, vegetable, or mineral, e.g., beeswax, lanolin, carnauba, and montan waxes), *petroleum* sources (e.g., paraffin waxes from crude oil), or *synthetic* sources (e.g., polyolefin and Fischer–Tropsch waxes).^{1,2}

The natural waxes contain oxygen functional groups, which give the waxes certain advantageous properties. The petroleum and synthetic waxes, on the other hand, are purely hydrocarbon waxes but are commercially oxidized by reaction at elevated temperatures with air or oxygen, thereby adding value to these waxes and making them suitable for other applications. Complex mixtures of oxygen functional groups generally result from such treatment, and it is usual to characterize the product by determination of the saponification number, a value which indicates the number of acid and ester groups in a substance. The saponification number (or value) is defined as the number of milligrams of potassium hydroxide required to hydrolyse 1 g of the sample and is a measure of the amount of saponifiable matter present. It is a particularly important parameter for users of oxidized waxes, both natural and synthetic, as ester functionality determines the utility of the wax, and the value itself constitutes a significant quality control test.

An ASTM method exists³ which involves refluxing the wax for a substantial time (over 3 h) with an excess of base (KOH) in ethanol. The excess KOH is determined by titration with HCl solution, whereafter the saponification value is determined from the amount of KOH consumed:



If the acid value has been previously determined (as is usually the case), the ester value may be calculated by subtracting the acid value from the saponification value.

Recently, we at Schumann Sasol Wax Research,⁴ in collaboration with the Microwave Chemistry Research Group at the University of Cape Town, have been investigating the use of microwaves for various purposes and have subsequently developed a method for determining saponification values using microwave heating. We have reduced the total analysis time from more than 3 h per sample to as little as 30 min for four samples (typically the number of samples our quality control laboratory desires to perform at any one time) by substituting microwave digestion for the conventional heating process and using methyl Cellosolve (2-methoxyethanol) instead of ethanol, the change in solvent being a modification introduced by Sasol several years ago.⁵

A preliminary account of this work was recently communicated.⁶ The reader is referred to a recent overview for general information on microwave dielectric heating effects and applications.⁷

Experimental Section

In the new method, the wax (1 g) is accurately weighed into a Teflon sample digester (100 cm³) fitted with a rupture membrane (bursting disk) system, commercially available from CEM Corp.⁸ Potassium hydroxide in methyl Cellosolve (30 cm³ of 0.1 mol dm⁻³) is added to the vessel by buret,

- (3) American Society for Testing and Materials. Standard Test Method for Saponification Number (Empirical) of Synthetic and Natural Waxes. ASTM method D1387-89; ASTM: Philadelphia, PA, 1989.
- (4) Schumann Sasol is a company formed in 1995 by merger of Sasol Waxes (the wax division of Sasol Ltd., Sasolburg) and Hans-Otto Schumann GmbH, a petroleum wax company based in Hamburg.
- (5) Sasol Analytical Method No. 2.72/92, August 1992.
- (6) Beigley, J. R.; Hutton, A. T.; McLean, W. D. Saponification Values of Waxes Using Microwaves Instead of Conventional Heating. Presented at the International Conference on Microwave Chemistry, Prague, Czech Republic, September 6–11, 1998; Poster P32.
- (7) Mingos, D. M. P.; Whittaker, A. G. Microwave Dielectric Heating Effects in Chemical Synthesis. In *Chemistry Under Extreme or Non-Classical Conditions*; van Eldik, R., Hubbard, C. D., Eds.; John Wiley & Sons and Spektrum Akademischer Verlag: New York and Heidelberg, 1997; Chapter 11, pp 479–514.
- (8) CEM Advanced Composite Vessel, from CEM Corp., P.O. Box 200, Matthews, NC 28106, USA.

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- (1) Warth, A. H. *The Chemistry and Technology of Waxes*, 2nd ed.; Reinhold Publishing Corp.: New York, NY, 1956.
- (2) Bennett, H. *Industrial Waxes*, 2nd ed.; Chemical Publishing Co.: New York, NY, 1975; Vol. 1.

and the vessel is closed. **Caution:** *Methyl Cellosolve (2-methoxyethanol) is poisonous!* Three other vessels are similarly prepared (with wax or as blanks—a blank result is necessary for calculation of the saponification value). The vessels are evenly placed on a carousel (also available from CEM Corp.), and the carousel is placed in the microwave oven.

We use a 1000-W domestic microwave oven,⁹ which has been modified on the basis of work by Pougnet.¹⁰ The modifications¹¹ entail replacing the control panel with new switchgear, which allows the power to be controlled in square-wave fashion (i.e., full power for x seconds, zero power for x seconds, alternating, with x being selectable). Experiment resulted in us using a periodicity of 4 s and a total time of 15 ± 1 min. The reason for the periodic application of power is to prevent the vessel from overpressurising. At the end of this time, the vessels are removed from the oven and placed in cold water for cooling. This takes about 5 min, until the vessels are sufficiently cool to be opened. **Caution:** *If the lid of the vessel is still tight, it should be cooled further to ensure that the pressure inside the vessel is the same as that outside.*

The solution is titrated in the vessel with aqueous 0.3 mol dm⁻³ HCl using phenolphthalein as indicator. As with the conventional method,³ the solution is titrated until it is nearly colourless. The vessels are then closed and placed back in the microwave oven for a further 5 ± 1 min. The vessels are removed from the oven, cooled again in water, and opened, and if the pink colour has reappeared, then the solution is again titrated until it is colourless. The titration values are added together, and calculation of the saponification value is as for the conventional method:³

$$\text{saponification value, mg KOH/g} = [(V_1 - V_2) \times M \times 56.1]/m$$

where V_1 and V_2 are the volumes of 0.3 mol dm⁻³ HCl used for the blank and sample, respectively, M is the molarity of HCl, 56.1 is the molar mass of KOH, and m is the mass of sample used in grams.

Results and Discussion

Samples of two different oxidized wax products, Paraflint A1 (an oxidized wax with a typical acid value of 27 mg of KOH/g) and Paraflint A2 (a saponified wax with a typical acid value of 12 mg of KOH/g),¹² were analysed by the

- (9) Sanyo model EM-V860, 1000 W. This multimode microwave oven incorporates a thermal cutoff switch in case of excessive reflected power returning to the magnetron, but in our experience of almost daily use over a period of more than a year, no problems in this regard have been encountered. The microwave-absorbing properties of the samples in the oven clearly will not necessarily be impedance-matched to the power source, but the samples (of which there are simultaneously four in the oven on a rotating turntable) are not dimensionally small and are expected to have significant dielectric loss tangents (see: Gabriel, C.; Gabriel, S.; Grant, E. H.; Halstead, B. S. J.; Mingos, D. M. P. *Chem. Soc. Rev.* **1998**, 27, 213), so it is not expected that a large amount of energy will be reflected back to the microwave source.
- (10) Pougnet, M. A. B. Design of Microwave Heating Equipment for Laboratory Applications. Ph.D. Thesis, University of Cape Town, 1993.
- (11) Details are available from the authors. Several manufacturers offer suitable microwave equipment, but we found the modification route to be the most cost-effective for our purposes.
- (12) Paraflint is a registered tradename of Schümann Sasol.

Table 1. Results of microwave versus conventional methods for determination of saponification values of Paraflint A1 and A2 waxes (units are mg of KOH/g)^a

Paraflint A1		Paraflint A2	
conventional	microwave	conventional	microwave
47.70	49.67	32.22	30.23
47.32	48.25	33.90	31.14
49.19	48.99	32.00	30.45
48.53	50.46	32.32	31.25
47.64	48.95	32.55	30.63
48.88	48.05	32.99	32.89
47.47	48.98	31.68	33.69
47.50	47.86	30.46	31.45
48.67	48.90	32.43	32.78
50.62	47.49	32.74	33.13
49.93	47.64	31.19	32.13
50.60	49.14	32.90	32.96
49.59	49.26	32.13	31.34
50.59	49.91	32.72	32.99
47.40	47.70	30.57	31.05
47.87	48.87	31.48	31.55
47.25	48.22	33.08	31.95
50.51	47.54	33.18	31.18
48.46	49.74	30.83	32.64
47.42	48.96	30.47	33.77
—	49.90	30.62	32.41
—	—	—	32.31
—	—	—	30.15
$n_c = 20$	$n_m = 21$	$n_c = 21$	$n_m = 23$
$\bar{x}_c = 48.66$	$\bar{x}_m = 48.78$	$\bar{x}_c = 32.02$	$\bar{x}_m = 31.92$
$s_c = 1.254$	$s_m = 0.873$	$s_c = 1.018$	$s_m = 1.082$

^a The subscripts c and m refer to the results obtained by the conventional and microwave methods, respectively.

conventional method and the microwave method at least 20 times. The results are shown in Table 1, where the calculated sample means and their standard deviations are also given.

We then used statistical hypothesis testing¹³ to confirm that the means of the results from each method were the same. The null hypothesis adopted was that the difference between the means of the results given by the two methods was zero (i.e., the means were equal). A two-tailed t test was used with a significance level of $P = 0.1$ (i.e., 90% confidence interval). This meant that there was a 10% chance we would reject our hypothesis when, in fact, it was true. There were 39 degrees of freedom for the Paraflint A1 data [42 for Paraflint A2].¹⁴ Using standard statistical formulas,¹³ a pooled estimate of the standard deviation can be calculated from the two individual standard deviations, s_c and s_m , giving $s = 1.076$ [1.052]. This value can then be used to find the standard error of the difference between the two means, giving $s_{\bar{x}(c)-\bar{x}(m)} = 0.336$ [0.318], whence the experimental value of $t = \bar{x}_c - \bar{x}_m/s_{\bar{x}(c)-\bar{x}(m)} = -0.357$ [0.314].

For both 39 and 42 degrees of freedom at a significance level of $P = 0.1$, the critical value of $|t|$ is 1.68;¹⁵ since the observed value of $|t|$ is less than this (for both waxes studied),

- (13) Miller, J. C.; Miller, J. N. *Statistics for Analytical Chemistry*, 2nd ed.; Ellis Horwood: Chichester, 1988.
- (14) In this discussion, the results for the analysis of the Paraflint A2 data are given in square brackets. The subscripts c and m refer to the results obtained by the conventional and microwave methods, respectively.
- (15) Spiegel, M. R. *Mathematical Handbook of Formulas and Tables*; Schaum's Outline Series; McGraw-Hill: New York, NY, 1968.

the null hypothesis is accepted: the means of the results given by the two methods are the same. We can confidently use the microwave method in the knowledge that the results are the same as those determined using the conventional method.

Although we have made no attempt to monitor or control the temperature or pressure within the vessels directly,¹⁶ the statistical analysis shows that the analytical results are reproducible, thus implying that the conditions inside the vessels are reproducible. The consequent simplicity of the method described is one of its attractive features.

The method is suitable for the determination of saponification values in waxy products in the range 0.1–100 mg of KOH/g. Organic chlorides, nitriles, and amides may be hydrolysed by the reagent and are possible sources of error. Ketones interfere only slightly, but aldehydes consume alkali and, therefore, interfere significantly if present in high concentration. However, these interferences are unlikely to be found in natural or synthetic waxes.

In conclusion, our results show that the microwave method for the determination of saponification value gives

the same results as using the conventional method, with repeatability and reproducibility at least the same as the ASTM method,³ though there is some evidence indicating that the microwave method has better repeatability. Additionally, the reduction in analysis time from more than 3 h per sample to as little as 30 min for four samples demonstrates the benefits of applying microwave technology in the analytical laboratory. This method is now in everyday use in the service laboratory (quality control) at Schümann Sasol.¹⁷

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(16) Kingston, H. M.; Jassie, L. B. Monitoring and Predicting Parameters in Microwave Dissolution. In *Introduction to Microwave Sample Preparation: Theory and Practice*; Kingston, H. M., Jassie, L. B., Eds.; American Chemical Society: Washington, DC, 1988; Chapter 6, pp 93–154.

(17) Schümann Sasol Analytical Method No. 023-98, March 1998.