Measurement of Fluoride Content in Toothpaste Application Note 5

Summary

- Fast, accurate, repeatable and non-destructive
- No sample preparation
- Simple linear calibration
- Easiest, most reliable technique available; suitable for unskilled personnel

Application

Modern toothpastes are designed to do more than just clean teeth. Hence, they contain many additives, either for health or for cosmetic reasons, such as components to prevent tooth decay, colorants, flavours and preservatives. Fluorine containing compounds (fluorides) are important additives of modern toothpastes as they protect the enamel by decreasing the number of bacteria and preventing demineralising of teeth. However, toothpastes are classified as drugs, not cosmetics, therefore the level of fluorides must be carefully controlled and measured accurately at different stages of production and product release.

Advantages of NMR

Conventional methods currently in use for determining the fluoride content such as titration, ion selective electrodes or ion chromatography are time consuming, require a trained analyst, and may involve the use of chemicals for changing the pH of the test solutions.

The **MQC+** benchtop Nuclear Magnetic Resonance (NMR) analyser offers a simple, non-destructive and rapid method for the measurement of fluoride concentration in toothpastes. NMR detects the soluble fluoride content in toothpastes, which is the most important parameter in determining its effectiveness in oral care. The two main fluorine based additives are sodium fluoride (NaF) and sodium monofluorophosphate (MFP). Most toothpastes contain between 0.05 and 0.15 weight-% (500 to 1500 ppm) of fluorides, a level that is easily detectable by NMR.

Although the oral care products can be either a gel or paste with a wide variety of additives, NMR does not exhibit significant change in performance with different formulas.

This method may be used for routine analysis in a production environment without any requirements for additional chemicals or specialist operator training.

Method

The analytical technique is based on direct measurement of the Nuclear Magnetic Resonance (NMR) signal of fluorine-19 which has 100% natural abundance. The acquired NMR signal is normalised by the sample mass and then the fluoride content (ppm) is calculated using an appropriate calibration curve.

Calibration

It is possible to calibrate the **MQC+** analyser using only two aqueous solutions of sodium fluoride. However, if a more advanced calibration is required, it is recommended that the instrument is calibrated by 3-6 (or more) standards with known fluoride content spread over the range of interest.

Figures 1 and 2 show NMR calibrations for adult (fluoride content 1200-1820 ppm) and children's (fluoride content 0-1000 ppm) toothpastes.

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Measurement of Fluoride Content in Toothpaste

Measurement

A tared sample vial is filled to a given height with a toothpaste sample, weighed, then transferred to a longer length tube prior to NMR analysis. The recommended measurement time for samples of adult products with sodium fluoride is 5 minutes per sample and for adult products containing MFP is 12 minutes per sample. For children's products, the recommended measurement times are 10 and 24 minutes per sample, respectively. The samples may be conditioned at 40°C for better repeatability.

Results

Table 1 compares the reference values of various toothpastes against the fluoride contents measured by NMR. Tables 2 and 3 demonstrate the repeatability and reproducibility of the NMR technique.

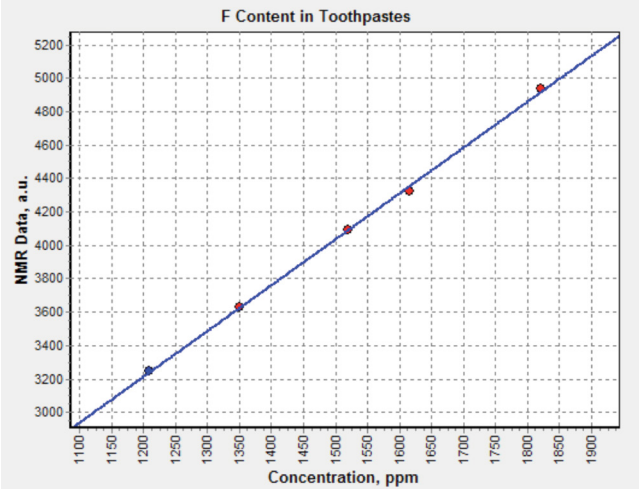

Figure 1: *NMR calibration for fluoride in adult toothpastes (R^2 = 1.000, SD = 7 ppm); aqueous sodium fluoride solutions were used as calibration standards.*

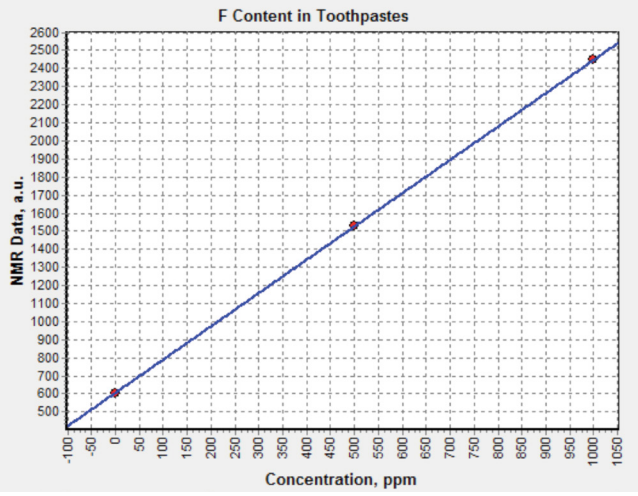

Figure 2: *NMR calibration for fluoride in children's toothpastes (R^2 = 1.000, SD = 2 ppm); aqueous sodium fluoride solutions were used as calibration standards*

Table 1. Comparison of the reference values of various toothpastes against the fluoride contents measured by NMR

Sample ID	Given F_{ref}, ppm	Predicted NMR F-content F_{NMR}, ppm	Difference (F_{ref}-F_{NMR}), ppm
1	500	505	-5
2	1000	1001	-1
3	1450	1446	+4

Table 2. NMR results for repeat measurements of the same sample of an adult toothpaste

Reference F-Content, ppm	Repeat NMR Measurements: F-Content, ppm					Mean F-Content, ppm	Standard Deviation, ppm
1447	1465	1445	1441	1452	1438	1448	11

Table 3. NMR results for different portions of the same adult toothpaste

Reference F-Content, ppm	F-Content in Different Toothpaste Portions by NMR, ppm					Mean F-Content, ppm	Standard Deviation, ppm
1410	1393	1422	1438	1413	1407	1415	17

Conclusion

- A primary calibration can cover the fluoride concentration range required in the industry, typically between 200 and 2000 ppm
- NMR is very stable over the long term and rarely needs re-calibration
- NMR techniques require minimal sample preparation without the use of solvents and other media
- NMR measurement precision is excellent compared to conventional methods
- Repeatability and reproducibility of the NMR method meet all industrial requirements for routine ^{19}F analysis
- Faster measurement and requiring much less operator time than conventional methods
- The NMR technique is non-destructive so the same samples may be measured several times before being analysed by other techniques.

Complete Package

Oxford Instruments offer a package especially tailored to the measurements of fluoride content in oral care products:

- Oxford Instruments **MQC+**F NMR Analyser
  - 0.55 Tesla (22 MHz) high homogeneity magnet
  - Probe for 26 mm diameter sample tubes (10 ml sample volume)
  - Integrated system controller (no external PC required)
  - Integrated flat-screen display
- **MultiQuant** software including **RI Calibration**, **RI Analysis**, and the **EasyCal** 'Fluoride Content in Toothpaste' application which guides the user through the calibration and analysis procedures
- Test/tuning samples
- Glass tubes with inserts for easy and fast sample preparation
- User manuals
- Method sheet

Optional items:

- A precision balance (3 decimal places)

visit **www.oxinst.com/mqc** for more information or email: **magres@oxinst.com**

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