# Analysis of Dairy Products, Using SIFT-MS

The sensory appeal of dairy products is in part due to the very desirable aromas that they exhibit. These aromas are most often due to volatile organic compounds (VOCs). In this White Paper we demonstrate some benefits of applying Selected Ion Flow Tube Mass Spectrometry (SIFT-MS) to analysis of a range of dairy products.

## Introduction

The world production of cow's milk was 480 million tonnes in 1999, with over 43% of this produced in Europe and nearly 20% in North and Central America.[1] Many different consumer products are produced from milk, such as cheese, yoghurt and butter, or use milk as an important ingredient, such as milk chocolate.

Good quality raw or low-temperature pasteurised fresh milk has a rather bland flavour.[2] The slightly sweet and salty taste arises from lactose and milk salts, and the weak aroma from a complex mixture of aroma compounds, most of which occur at concentrations less than the flavour threshold. The rather weak and bland flavour of milk means that it is very susceptible to undesirable modification. Cheese manufacture, for example, typically requires use of the highest sensory quality milk to avoid undesirable flavours in the end product.

Volatile organic compounds (VOCs) are very important contributors to the characteristic aromas and aroma defects perceived in milk and its products.[3-5] In this document we discuss the application of SIFT-MS to detection of volatile aroma compounds in a range of dairy products. Results from a range of actual SIFT-MS analyses are presented.

## Volatile Aroma Compounds in Milk and Its Products

As mentioned above, milk has a rather bland flavour when fresh and of good quality. Due to the very low levels of compounds contributing to the aroma, it has proved difficult to definitively identify the most important constituents. It appears that some of the more important ones in low-temperature pasteurised milk[6] are dimethylsulfide, diacetyl (2,3-butanedione), 2-methylbutanal, (Z)-4-heptenal, 3-butenylisothiocyanate and (E)-2-nonenal. Higher temperature heat treatments, which extend the shelf-life of the milk, tend to result in a cooked flavour from sulfur compounds, such as hydrogen sulfide, produced by protein breakdown. Ketones and lactones are also produced. Sterilisation of the milk at even higher temperatures leads to marked chemical changes, producing browning and Maillard reaction products (e.g. the furanones, including maltol), as well as the ultra heat treated (UHT)-like products.

A large number of other flavour defects can occur in milk, including those from:

- Milk production in the cow itself (e.g., due to metabolic disturbances, infections, or taints from feed)
- Improper handling and storage of milk after the cow is milked
- Contamination of the product during processing
- Taints from packaging or other odorous products stored nearby.

Table 1 lists a number of milk defects and the associated volatile compounds causing them.[7].

**Table 1.** *Flavour defects in milk and the compounds that contribute to them (adapted from Ref. 7).*

| Flavour Defect | Contributing compounds |
|---|---|
| Feed flavour | Dimethyl sulfide, acetone, butanone, ethanol, 1-propanol, 2-propanol |
| Weed taints | Methyl mercaptan, dimethyl sulfide, dimethyl disulfide, indole, skatole |
| Cowy flavour | Dimethyl sulfide, acetone |
| Putrid flavour | Methyl mercaptan, dimethyl sulfide, dimethyl disulfide |
| Unclean flavour | Dimethyl sulfide |
| Cooked flavour | Hydrogen sulfide, methyl mercaptan, dimethyl sulfide, dimethyl disulfide |
| Heating flavour (sterilisation / caramelisation) | Maltol, furaneol, 2,5-dimethylpyrazine, 2-aminoacetophenone, 2-pentanone, 2-heptanone, 2-nonanone, 2-undecanone |
| Heating flavour (UHT ketone-like) | 2-Pentanone, 2-heptanone, 2-nonanone, 2-undecanone |
| Light-induced flavour (activated) | Methyl mercaptan, dimethyl sulfide, dimethyl disulfide, 3-methylthiopropanal |
| Oxidation flavour (general) | Acetone, butanone, 2-pentanone, 2-heptanone, 2-nonanone, 2-undecanone, hexanal, heptanal, octanal, nonanal, decanal |
| Oxidation flavour (metallic) | Methyl vinyl ketone, ethyl vinyl ketone, amyl vinyl ketone |
| Oxidation flavour (tallowy) | Hexanal, heptanal, octanal, nonanal, decanal, 2-heptenal, 2-octenal, 2-nonenal, 2-decenal |
| Oxidation flavour (green, cucumber) | 3-Hexenal, 2,6-nonadienal |
| Oxidation flavour (fatty, fried) | 2-heptenal, 2-octenal, 2-nonenal, 2-decenal, 2,4-heptadienal, 2,4-decadienal |
| Oxidation flavour (fishy) | 2,4,7-Decatrienal |
| Malty flavour | 2-Methyl propanal, 2-methyl butanal, 3-methyl butanal |
| Acid flavour | Acetic acid, lactic acid |
| Lypolytic rancidity | Butanoic acid, pentanoic acid, hexanoic acid |
| Fruity flavour | Butanoic acid, hexanoic acid, ethyl butanoate, ethyl 3-methylbutanoate, ethyl hexanoate |

### *Cheese*

The microbial processes occurring during the production of cheeses yield a diverse range of volatile aroma compounds which are generally at higher concentrations than in milk. As of 1991, 213 compounds had been identified in the headspace of cheddar cheese.[8] Fermentation produces the volatile fatty acids ($C_2$-$C_6$), lactic and succinic acids. Esters, ketones, small branched aldehydes and sulfides are often observed at lower concentrations, although the presence and levels of these vary depending on the type of cheese[9,10] due to the particular microbe(s) used to prepare it.

### *Yoghurt and other sour milk products*

The lactic acid bacteria used to create yoghurt produce a variety of compounds that contribute to its aroma. These compounds include acetaldehyde, diacetyl, dimethyl sulfide, acetic acid, lactic acid, 1-octen-3-one and 1-nonen-3-one.[11] Acetaldehyde and diacetyl dominate the aromas of other sour products, because they are also produced by the action of lactic acid bacteria.

### *Butter*

The aroma of butter is dominated by three VOCs: diacetyl, butanoic acid and δ-decalactone.[12] A rather delicate balance between these volatiles must exist for the butter to maintain a favourable aroma.

## SIFT-MS and Its Suitability for Detection and Quantitation of Dairy VOCs

SIFT-MS is a powerful analytical technique that uses chemical ionisation reactions coupled with mass spectrometric detection to rapidly quantify targeted VOCs. VOCs are identified and quantified in real time from whole-gas samples based on the known rate coefficients for reaction of the chemically ionising species (so-called reagent ions) with the target analytes.

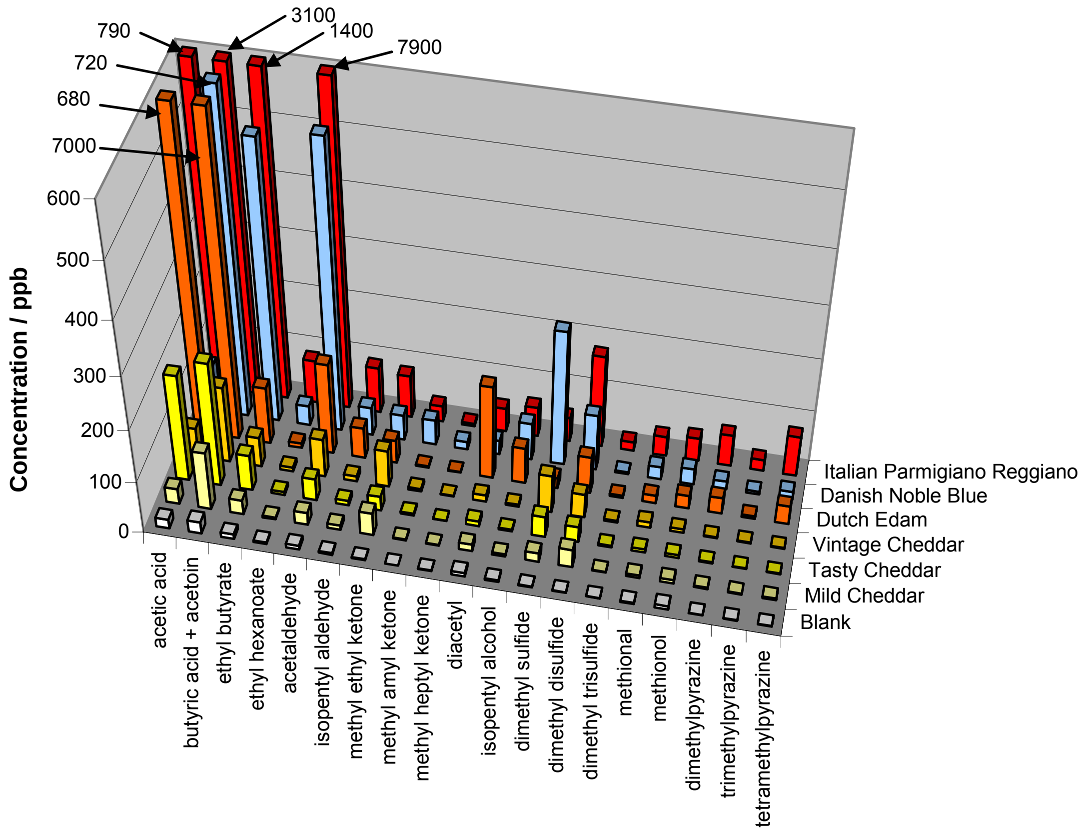
The most common reagent ions used are $H_3O^+$, $NO^+$ and $O_2^+$, which react with trace VOCs in well characterised ways but *do not* react with the major components of air. Generally the soft chemical ionisation used in SIFT-MS yields a smaller range of product ions than is common in electron impact mass spectrometry (as used by gas chromatography mass spectrometry (GC-MS), for example). Hence the need for gas chromatographic separation of the sample is circumvented, speeding sample throughput and providing instantaneous quantification of VOCs. Use of several reagent ions to independently quantify target analytes also greatly reduces interferences, markedly increasing the specificity of SIFT-MS versus competing whole-gas analysis technologies.

These characteristics make SIFT-MS ideally suited to rapid, sensitive detection and quantification of the volatile aroma compounds in milk and its products that have been outlined in the preceding section. SIFT-MS is also well-suited to detection of added flavours. Several examples of the application of SIFT-MS to dairy products are given below. Unless otherwise stated, Syft Technologies Voice100™ SIFT-MS instruments were used for this work.

### *Cheese*

The headspaces of a range of cheeses have been analysed using SIFT-MS, key results of which are summarised in Figure 1. Of particular interest here are the elevated methyl ketones, diacetyl and ethyl butyrate that are characteristic of blue, Edam and Parmigiano Reggiano cheeses, respectively.

**Figure 1.** Headspace concentrations (37 °C) of VOCs found in 50-gram samples of New Zealand cheddar cheeses and 40-gram samples of European speciality cheeses, using SIFT-MS.




***Yoghurt and other sour milk products***

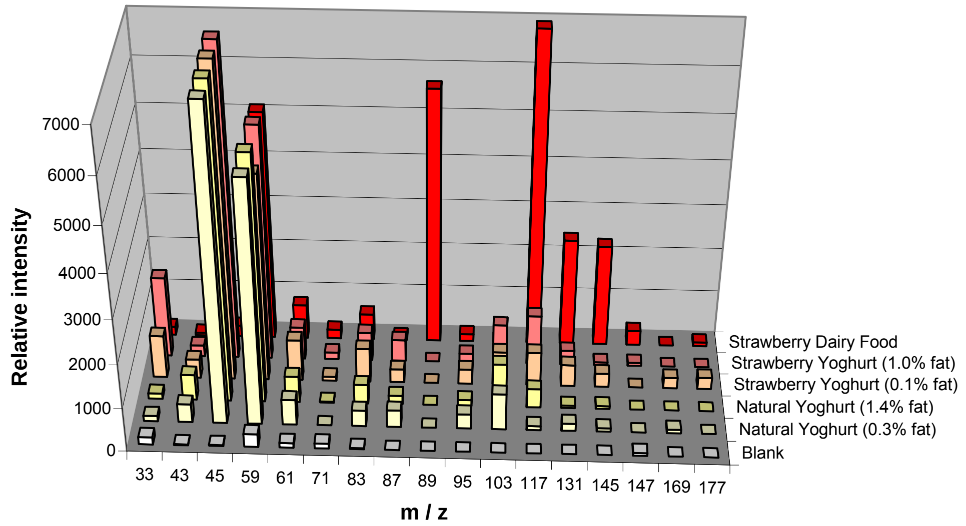
Figure 2 presents reduced mass scans of 15-gram samples of several New Zealand yoghurts for each of the three standard reagent ions used in SIFT-MS ($H_3O^+$, $NO^+$ and $O_2^+$). The use of three reagent ions allows SIFT-MS to have greater certainty in the identification of compounds than is possible using just one reagent ion. It also resolves much compound interference, allowing more confident quantitation of the target compound.

The difference between the strawberry yoghurts and the strawberry dairy food is of particular interest in the mass spectra. The latter uses a synthetic flavour, and its profile is dominated by $C_4$, $C_6$, $C_7$ and $C_8$ esters, whereas the former use fruit (plus some additional flavour). The levels of esters in the strawberry yoghurt are much lower, but are nevertheless readily detectable.

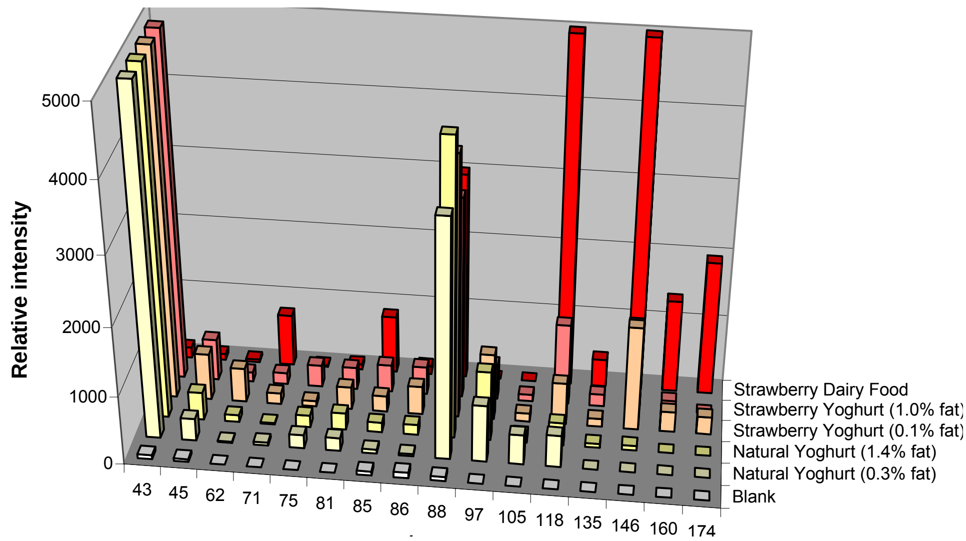
Figure 3 gives quantitative data for the more abundant, natural volatiles present in yoghurt. The dominant volatile is acetaldehyde, which occurs in the ranges 35 to 37 ppm and 24 to 27 ppm for the natural and the flavoured (strawberry and vanilla) yoghurts, respectively.

**Figure 2.** Headspace mass spectra (22 °C) of natural and strawberry-flavoured (fruit plus additional flavour) yoghurts and a strawberry-flavoured dairy food (all of New Zealand origin), using the (a) $H_3O^+$, (b) $NO^+$ and (c) $O_2^+$ reagent ions of SIFT-MS.

a) $H_3O^+$




b) $NO^+$




c) $O_2^+$

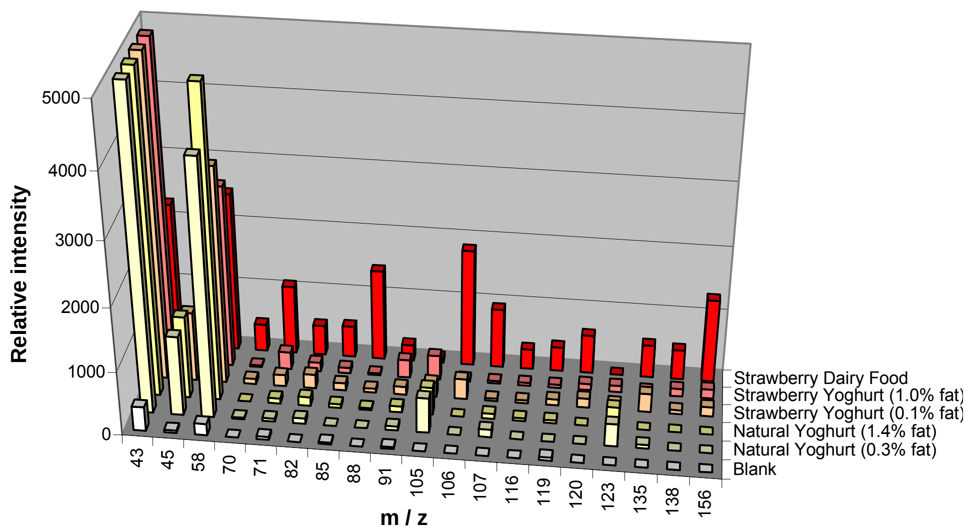
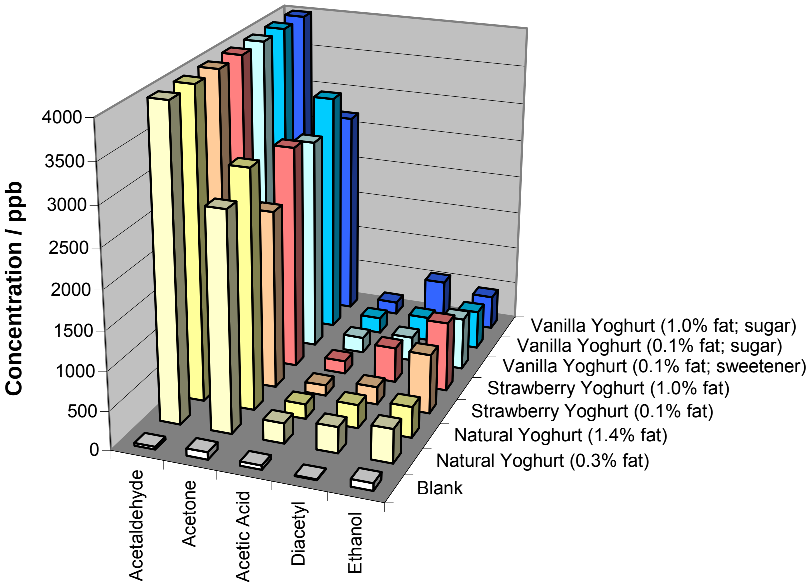


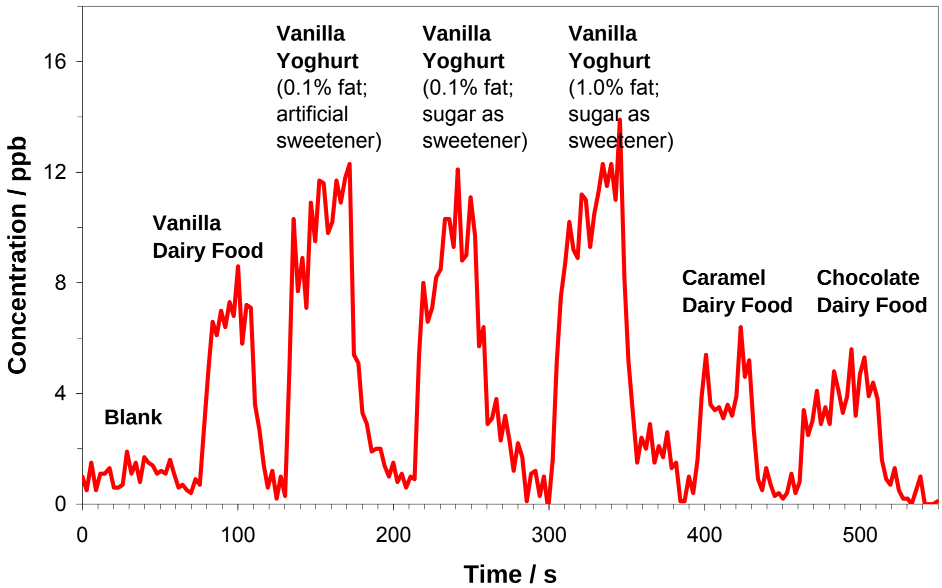
**Figure 3.** Headspace concentrations (22 °C) of non-additive flavour compounds in several New Zealand yoghurts, using SIFT-MS.




### *Flavoured dairy products*

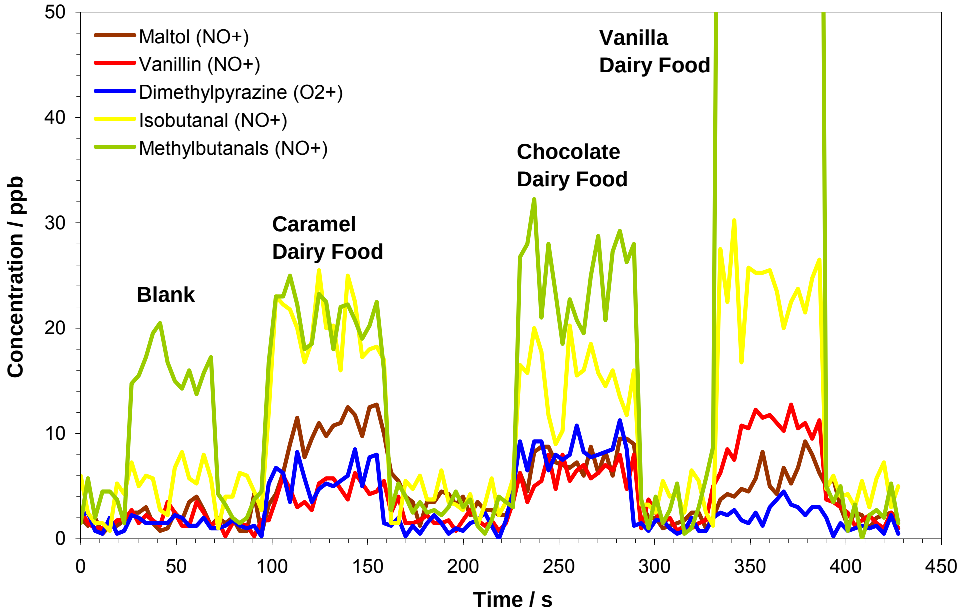
Yoghurts and dairy foods (custard-like products) commonly have artificial flavours added to them to provide additional sensory appeal appeal to the consumer. Vanilla is an extremely important flavour compound with a small, but measurable vapour pressure. In Figure 4 we show the results of SIFT-MS analysis (Syft Technologies Ltd, Voice200$^{TM}$ SIFT-MS instrument) of the headspace of several yoghurts and dairy foods for vanillin. In these experiments, analysis was performed from open 250-mL Schott bottles containing 50 grams of dairy food.

**Figure 4.** Headspace concentrations (ca. 30 °C) of vanillin in vanilla-flavoured yoghurts and several flavoured dairy foods (all of New Zealand origin), using SIFT-MS.




Maltol is the recognised caramel standard in the food industry and it also occurs in chocolate. Figure 5 demonstrates detection of maltol and other flavour compounds in the headspace of three dairy foods under similar conditions to those used for the data in Figure 4.

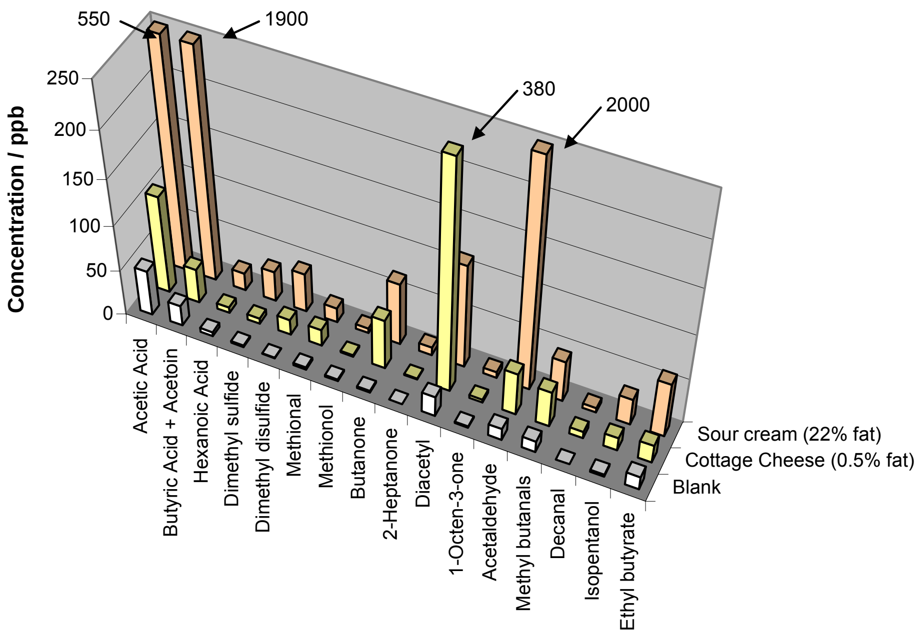
**Figure 5.** Concentrations (ca. 30 °C) of some important flavour compounds in the headspace of several flavoured dairy foods (all of New Zealand origin), using SIFT-MS.




### *Other Dairy Products*

Figure 6 shows the volatiles detected and quantified by SIFT-MS in the headspace above 50-gram samples of a New Zealand cottage cheese (0.5% fat) and sour cream (22% fat). The sour cream shows the diacetyl, acetaldehyde, dimethyl sulfide and acetic acid that are characteristic of the lactic acid bacteria used to sour it.[11] Cottage cheese exhibits lower levels of most VOCs, and is dominated by diacetyl.

**Figure 6.** Headspace concentrations (22 °C) of a variety of dairy product-related VOCs found in low fat cottage cheese and standard sour cream (both of New Zealand origin), using SIFT-MS.



## Summary

Dairy products are diverse in their natural flavours and, consequently, in the volatile profiles that they exhibit. Additional flavours (whether natural or synthetic) are often used to further modify the aroma of the dairy product.

SIFT-MS is a very sensitive, rapid and specific tool that has benefits for detection of favourable and unfavourable aromas in a wide range of dairy products. It is readily configurable for applications as diverse as on-line product quality assessment and research laboratory applications.


Further information on SIFT-MS, including background, technical and application specific information, is available on the Syft Technologies website www.syft.com. Alternatively, questions and enquiries can be sent directly to info@syft.com.

## References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