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# Extraction of lipids from a specialist dairy stream

O.J. Catchpole [a,*], S.J. Tallon [a], J.B. Grey [a], K. Fletcher [b], A.J. Fletcher [b]

[a] *Industrial Research Limited, P.O. Box 31-310, Lower Hutt, New Zealand*
[b] *Fonterra Research Centre, Private Bag 11029, Palmerston North, New Zealand*

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**Abstract**

In this work a process for the extraction of neutral and complex lipids from the specialist dairy stream 'beta-serum' is described. Beta-serum is a proprietary product obtained from dairy streams containing greater than 60% fat that have been through phase inversion from an oil-in-water to a water-in-oil emulsion. It is an enriched source of milk fat globular membrane proteins and complex lipids, and is distinct from buttermilk in this respect. In the process described here a total lipid extract could be obtained from liquid beta-serum using a continuous near-critical dimethyl ether (DME) antisolvent fractionation process. Protein and water are precipitated from solution when mixed with the DME, whilst lipid and some water are extracted into the DME-rich phase. The extraction yield of lipids depended on the solids content of the feed and the feed to DME flow ratio, but did not depend on the lactose content. Lipids were also extractable from spray dried beta-serum powder, but only when the lactose content had been reduced below 45% by mass. A two step extraction process is described in which neutral lipids are extracted with supercritical $CO_2$, and then polar lipids using near-critical DME. The polar lipid extract was enriched in phospholipids (~70% by mass), which included phosphatidylcholine, phosphatidylethanolamine, phosphatidylinositol, phosphatidylserine, and sphingomyelin. Other complex lipid components extracted included gangliosides and cerebrosides. Unlike the antisolvent process, proteins were not denatured during either $CO_2$ or DME processing of the spray dried powders, and the de-fatted powders are therefore suitable for a range of functional foods. A polar lipid extract could also be produced from spray dried powder by extracting first with DME to obtain a mixed neutral/complex lipid extract, then re-extracting the lipid extract with $CO_2$ to remove neutral lipids.


*Keywords:* Dairy; Protein; Lipid; Phospholipid; Extraction; Fractionation; Dimethyl ether; Near critical; Antisolvent

## 1. Introduction

Supercritical $CO_2$ is the most widely used near-critical fluid for the extraction of lipids. However, $CO_2$ cannot extract complex lipids unless an organic co-solvent is also used. Among the other near- and super-critical fluids that could be considered, we have found that dimethyl ether (DME) is a strong solvent for both neutral and polar lipids and has a wide range of potential use in food, pharmaceutical, and cosmetic applications. DME is non-toxic, non-reactive, does not cause a pH change in aqueous solution, and has a sufficiently high vapour pressure at room temperature that virtually complete solvent removal can be carried out easily and at moderate, or ambient, temperatures. In previous work, Yano et al. [1] claim a method for extracting 30–70% of the phospholipids and most of the cholesterol from freeze dried whole eggs using sub-critical DME. Bausch et al. [2] show that β-carotene forms a single phase at 33% by weight concentration in DME, and describe a process for spraying solutions of β-carotene in DME through a nozzle to form a dry particulate product. The solubility of several pharmaceutical compounds, including Orlistat and Saquinavir were also shown to exceed 10 wt%. Catchpole et al. [3] describe the extraction of oils from spices using DME, including ginger, black pepper, and chilli powder, and describe near-complete yields of oleoresin and essential oil components along with co-extracted water. DME is also commonly used as an aerosol propellant, particularly for oil-based formulations, in personal care products and crop sprays. To the knowledge of the authors no applications for use of DME in food processing have yet been finalised, but no barriers to its adoption are anticipated.

DME is also partially miscible with water, with a solubility of water in DME of between 10 and 20 mole%, and solubility of DME in water between 20 and 30 mole%, for pressures up to 100 bar and temperatures up to 333 K, as reported else-

* Corresponding author.
*E-mail address:* o.catchpole@irl.cri.nz (O.J. Catchpole).

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where [4–6]. This advantage of partial miscibility is not shared by other solvents such as propane and $CO_2$. It allows extraction using water as a co-solvent and extraction of both lipids and some water soluble compounds. Catchpole et al. [6] show that the solubility of phospholipids (soy lecithin) is at least 20 mass% at 333 K in DME, and increases to around 30 mass% with water as a co-solvent. Yano et al. [7] describe the use of DME and water mixtures to extract dried spices, teas, and fruits. The partial miscibility of DME with water also allows wet or liquid aqueous based feed streams to be extracted directly with DME, and removes the need for pre-drying of the feed material—a process that can be costly and/or involve processing conditions that may degrade the material being processed. Yano et al. [8] describe a process for extracting phospholipids directly from fresh egg yolks without pre-drying. Egg yolks were contacted in a batch process with DME and lipid (lecithin) extract yields were reported to be greater than those obtained with methanol or acetone. Yano et al. [8] state that denaturation of the residual protein fraction was observed when the fresh egg yolks were used, but the phospholipid extraction yield was greater than when dried egg was processed.

A continuous process for extraction of egg yolks and aqueous whey protein concentrate streams is described by Catchpole et al. [6] and Fletcher et al. [9]. In this process, the liquid feed stream is contacted with a continuous flow of DME through an in-line static mixer. The mixture then passes into a phase separation vessel from which a DME rich phase containing extracted lipid and water is taken off the top of the vessel, and excess water and residual solids are taken off the bottom. Lipid extraction ranges from 60% of available lipids through to greater than 90%, depending on the feed material and the processing conditions. Extraction efficiency was shown to depend on the feed solids concentration, feed lipid content, feed pH, temperature and DME-to-feed liquid flow rate ratio. All major phospholipids in the feed material were extracted, including phosphatidylcholine (PC), phosphatidylinositol (PI), phosphatidylethanolamine (PE), phosphatidylserine (PS), and sphingomyelin (SM).

Residual defatted protein streams from the continuous liquid extraction process were observed to have reduced levels of protein solubility after processing, indicating denaturation of the proteins. Catchpole et al. [6] show that for egg yolk proteins, the decrease in protein solubility depends on the processing temperature, pre-processing method, and the quantity of excess water. A greater loss of protein solubility was observed at higher temperatures, but also when there was only a small excess of water volume in the raffinate, or lower aqueous phase. Pre-saturation of DME with water before contacting with the feed stream has been shown to reduce the extent of protein solubility loss [6], and this also improves continuous recovery of the lower (raffinate) water phase by keeping the proteins in solution.

In this work we describe extraction of a specialist dairy stream, 'beta-serum', using DME in a batch process for the extraction of dry powders, and in a continuous process for extraction of liquid beta-serum with DME and water. The effect of reducing the lactose content on extraction of spray dried powder is investigated, and the effect of the dry batch and wet continuous processing on whey protein solubility is determined. This process is also further described by Fletcher et al. [10].

## 2. Experimental

### 2.1. Materials

Aerosol grade dimethyl ether (>99.5% DME by mass) was supplied by DAMAR Industries NZ Ltd. Beta-serum powders and solutions were produced and supplied by Fonterra Innovation, New Zealand.

Beta-serum [10] is a proprietary product obtained as a by-product from dairy streams containing greater than 60% fat that have been through phase inversion from an oil-in-water to a water-in-oil emulsion. Beta-serum is an enriched source of milk fat globular membrane proteins and complex lipids, and is distinct from buttermilk which has relatively low levels of complex lipids. The powder provided for this work had a total lipid content of 19.7%, including 7.9% phospholipids.

Table 1
Composition of feed powders used

| Component (wt%) | Beta-serum feed powders | | | | |
|---|---|---|---|---|---|
| | DME antisolvent extractions | '45%' lactose powder | '14%' lactose powder | '8%' lactose powder | '1%' lactose powder |
| Protein | 48.5 | 29.4 | 48.3 | 52.0 | 55.4 |
| Lactose | 11.0 | 42.5 | 14.4 | 7.8 | 0.6 |
| Ash[a] | 4.8 | 6.0 | 4.8 | 4.8 | 5.1 |
| Moisture | 3.2 | 3.1 | 3.0 | 2.7 | 2.3 |
| Total Fat | 34.8 | 19.7 | 30.1 | 31.9 | 39.1 |
| Total Phospholipid | 14.7 | 7.9 | 12.9 | 13.8 | 16.8 |
| Phosphatidylcholine | 4.0 | | | | |
| Phosphatidyinositol | 1.1 | | | | |
| Phosphatidylserine | 1.6 | | | | |
| Phosphatidylethanolamine | 4.2 | | | | |
| Sphingomyelin | 3.6 | | | | |
| Total Ganglioside | 2.4 | | | | |

[a] Includes phosphates from the phospholipid fraction.