OPTO-THERMAL SKIN WATER CONCENTRATION GRADIENT MEASUREMENT

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ABSTRACT

Opto-Thermal Transient Emission Radiometry (OTTER) has been shown to be able to measure stratum corneum hydration *in-vivo*. We now present a study that shows how the technique can be extended to give information about the distribution of water within the stratum corneum. This depth profile measurement capability is based on a new theoretical expression for the opto-thermal signal that takes a gradient of water concentration explicitly into account. The technique is illustrated with measurements on untreated skin and skin treated with petroleum jelly and DMSO.

Key words: Photothermal radiometry, hydration, stratum corneum, hydration profile.

1. INTRODUCTION

The stratum corneum is the outermost layer of the skin, which provides a barrier that protects the body from both desiccation and external invasions. Since the water content in the stratum corneum plays a crucial role in maintaining this barrier function, as well as the cosmetic properties of skin, the measurement (especially *in-vivo*) of stratum corneum hydration is very important.

Various *in-vivo* techniques have been used for skin water content measurement ¹, namely electrical measurements^{2, 3}, evaporimetry⁴, infrared spectroscopy ⁵, photoacoustic spectroscopy ⁶ and photothermal imaging ⁷. Recently OTTER (Opto-Thermal Transient Emission Radiometry) has demonstrated its capability for measuring skin hydration *in-vivo* ⁸. Compared with the other techniques, OTTER has the advantages of non-contacting measurement of a well defined thickness of stratum corneum, and it is quick to use.

Water distribution within the stratum corneum is not uniform, however. Near the surface, where the cells are in equilibrium with the environment, the stratum corneum is dryer; at its base, where the cells are in equilibrium with the moist part of the epidermis, the stratum corneum is wetter ^{6, 9}. Thus there exists a water concentration gradient within the stratum corneum. OTTER has the potential for sensing this hydration profile. It can be used with wavelengths of excitation and thermal emission that determine the desired depth of stratum corneum contributing to the measurement. The shape of the opto-thermal decay curves so measured is then determined by the optical and thermal properties of the stratum corneum within this depth. If these properties are not uniform, then the decay curves will deviate from the

mathematical model of a homogeneous material ¹⁰. It is observations of such deviations in the least squares analysis of opto-thermal decay curves that have led to the development of the new mathematical model for analysing stratum corneum hydration decay curves presented here.

2. THEORY

To a first approximation, the stratum corneum can be treated as a semi-infinite homogeneous material, in which case the opto-thermal decay signal has the form 10

$$S(t) = \frac{\mathbf{z} E_0 \mathbf{a} \mathbf{b}}{C\mathbf{r}(\mathbf{b}^2 - \mathbf{a}^2)} \left\{ \mathbf{b} e^{\mathbf{a}^2 D t} \operatorname{erfc}(\sqrt{\mathbf{a}^2 D t}) - \mathbf{a} e^{\mathbf{b}^2 D t} \operatorname{erfc}(\sqrt{\mathbf{b}^2 D t}) \right\}$$
(1)

where a is the absorbance for the excitation radiation, b is the absorbance for the thermal emission radiation, C the specific heat, r the density, D the thermal diffusivity, and E_0 the energy density absorbed from the excitation pulse. The parameter z includes factors that depend on the black body emission curve, detector sensitivity, focusing and alignment, but are independent of the properties of the sample *per se*.

For stratum corneum hydration measurements using Q-switched 2.94 μ m Er:YAG radiation for excitation, the saturation condition a >> b applies and Eq(1) reduces to

$$S(t) \approx \frac{\mathbf{z} E_0 \mathbf{b}}{C \mathbf{r}} e^{t/t} \operatorname{erfc}(\sqrt{t/t})$$
(2)

where $t = 1/b^2 D$ is the characteristic opto-thermal decay time, which can be related to mean fractional volume hydration, H, through $H \approx 0.9 t_{FH} / t$, where t_{FH} is the opto-thermal decay time for fully hydrated stratum corneum, thought to have $H \approx 0.9$. From prior experiments, $t_{FH} \approx 30 \text{ ms}$ at 6.05µm wavelength, $t_{FH} \approx 300 \text{ ms}$ at 13.1µm wavelength ⁸.

The assumption of homogeneity in the above model is justified as long as the characteristic penetration depth of the measurement, $\langle z \rangle$, estimated from ¹⁰

$$\frac{1}{\boldsymbol{a}+\boldsymbol{b}} < \langle z \rangle < \frac{1}{\boldsymbol{b}} \tag{3}$$

is less than the thickness of the stratum corneum. This is achieved in practice by selecting the wavelength of detection to maximise **b**. In pure liquid water, for example, $\langle z \rangle \approx 2 \mathbf{m} n$ at 6.05µm wavelength and $\langle z \rangle \approx 4 \mathbf{m} n$ at 13.1µm wavelength.

However, even if the measurement is confined to the stratum corneum, the assumption of homogeneity is unjustified. The outer layer of the stratum corneum is in contact with atmospheric air, where the water concentration will depend on atmospheric temperature and humidity. The base of the stratum corneum is in contact with the living cells of the epidermis and is likely to be fully hydrated. A first approximation to such a concentration profile is a linear model (Figure 1), i.e.

$$H(z) = H_0 + wz \qquad \qquad 0 \le z \le L_{sc} \tag{4}$$

where H(z) is the fractional volume hydration within the stratum corneum, H_0 is the hydration at the surface, w is a gradient, L_{sc} is the thickness of the stratum corneum and z is the distance beneath the stratum corneum surface, with z = 0 at the surface.



Figure 1. Water concentration profile within skin and its mathematical model.

It is not possible, however, to derive a closed form solution for the opto-thermal signal, even for such a simple hydration distribution, because the optical (a, b) and thermal (D, effusivity) properties of such a material would all vary with depth. An approximate solution can be derived, however, by making the following simplifying assumptions:

a) Thermal wave reflections within the material can be neglected, because there are no sharp boundaries within it.

- b) Changes of D can be neglected in comparison with changes of \boldsymbol{b} , because opto-thermal decay rates depend on the first power of D, but on the second power of \boldsymbol{b} .
- c) The thickness of the stratum corneum can be taken as infinite, i.e. $L_{SC} \rightarrow \infty$, as long as the depth of measurement is small by comparison.

The thermal diffusion equation for one-dimentional heat flow and impulse excitation is

$$\frac{\P \boldsymbol{q}(z,t)}{\P t} - D \frac{\P^2 \boldsymbol{q}(z,t)}{\P z^2} = \frac{E_0 \boldsymbol{a}}{k} e^{-\boldsymbol{a} z} \boldsymbol{d}(t)$$
(5)

where q(z,t) is the time-dependent change of temperature of sample and k the thermal conductivity. The solution for an insulating boundary at the surface is

$$\boldsymbol{q}(z,t) = \frac{\boldsymbol{z} E_0 \boldsymbol{a}}{2C \boldsymbol{r}} e^{\boldsymbol{a}^2 D t} \left\{ e^{-\boldsymbol{a}z} erfc(\frac{\boldsymbol{a}^2 D t - \frac{1}{2} \boldsymbol{a}z}{\sqrt{\boldsymbol{a}^2 D t}}) + e^{\boldsymbol{a}z} erfc(\frac{\boldsymbol{a}^2 D t + \frac{1}{2} \boldsymbol{a}z}{\sqrt{\boldsymbol{a}^2 D t}}) \right\}$$
(6)

The thermal emission decay (or OTTER) signal is given by ¹¹

$$S(t) = \frac{\mathbf{Z} E_0}{\mathbf{r}C} \int_0^\infty \mathbf{b}(z) e^{-\int_0^z \mathbf{b}(z) dz} \mathbf{q}(z, t) dz$$
(7)

where $\boldsymbol{b}(z)$ is taken as

$$\boldsymbol{b}(z) = \boldsymbol{b}_0 + wz \tag{8}$$

 \boldsymbol{b}_0 is the emission absorbance of the skin's surface and w is the gradient of the emission absorbance inside skin. Eq(7) can be solved with the profile of Eq(8) in the limit of saturated excitation, i.e. $\boldsymbol{a} >> \boldsymbol{b}$, to give

$$S(t) = \frac{\mathbf{z} E_0 \mathbf{b}_0}{\mathbf{r}C} \times \begin{pmatrix} \frac{2W\sqrt{t\mathbf{t}}}{\sqrt{\mathbf{p}} (2Wt+1)} + \\ \frac{1}{\sqrt{(2Wt+1)^3}} e^{\frac{t/t}{2Wt+1}} erfc(\frac{\sqrt{t}/\mathbf{t}}{\sqrt{2Wt+1}}) \end{pmatrix}$$
(9)

Where **t** is surface lifetime, defined by $\mathbf{t} = 1 / \mathbf{b}_0^2 D$, and W is the effective gradient, i.e. W = wD.

Eq(9) is the general solution for the opto-thermal signal of a semi-infinite optical gradient material in the limit of saturated excitation. It reduces to a semi-infinite homogeneous model, Eq(2), when $w \to 0$. In the other limit, $w \to \infty$, Eq(9) correctly reduces to the semi-infinite opaque model,

$$S(t) = \frac{\mathbf{z} \ E_0}{\mathbf{r}C} \times \sqrt{\frac{1}{D\mathbf{p}t}}$$
(10)

The dependence of Eq(9) on W is illustrated in Figure 2.



Figure 2. The theoretical opto-thermal signal at different effective gradient. The effective gradients are 0, 500, 1000, and 2000 s⁻¹ respectively.

Measured value of t and W can be converted to water content, if a linear relationship with emission absorbance is assumed, i.e.

$$\boldsymbol{b}_{H} = H \times \boldsymbol{b}_{w} + (1 - H) \times \boldsymbol{b}_{d}$$
(11)

where \boldsymbol{b}_{H} is the emission absorbance of skin of fractional volume hydration H, \boldsymbol{b}_{w} is the emission absorbance of water, \boldsymbol{b}_{d} is the emission absorbance of dry skin.

3. RESULTS

The experiments were divided into two parts: untreated skin, and skin treated with an external substance. In the first part, measurements were performed on four different skin sites, in order to explore changes of stratum corneum properties. The second part used topical applications of petroleum jelly and dimethyl sulphoxide (DMSO), to discover how these substances change the skin hydration profile. The measured opto-thermal decay curves were analysed using Eq (9) in a non-linear least-squares fitting program.

3.1 Untreated skin

Four different skin sites were selected: the ventral surface of the second finger, the dorsal surface of the second finger, lower part of the volar forearm and the upper part of the volar forearm. Measurements were performed using a detection wavelength of $13.1\mu m$.



Figure 3. The water hydration distribution within the Stratum Corneum at different skin sites.

The results are illustrated in Figure 3, where a is the upper part of the volar left forearm, b the lower part of the volar left forearm, c the dorsal surface of 2nd left finger, and d the ventral surface of 2nd left finger. The parameters used in the calculation are $\boldsymbol{b}_W = 2.9 \times 10^5 \, m^{-1}$, $\boldsymbol{b}_d = 1 \times 10^5 \, m^{-1}$ and $D = 6 \times 10^{-8} \, m^2 \, s^{-1}$.

The surface hydration is at its maximum on the upper forearm and very low on the finger, presumably reflecting the degree of exposure of the different sites to environmental influences. The gradients appear to increase with surface hydration. There may well be a relationship between gradient and stratum corneum thickness, since the same boundary condition apply, irrespective of thickness, i.e. the thicker the stratum corneum, the lower the average hydration gradient. This relationship is unlikely to be simple, however, especially when considering the very similar profile for the dorsal and ventral surface of the finger, despite their large difference of thickness and other properties. Measurements at 6.05µm wavelength give a much higher gradient than at 13.1µm wavelength at all sites tested. This is evidence of a non-linear water distribution within the stratum corneum, because the

mean radiation depth, $\langle z \rangle$, at 6.05µm wavelengths is smaller than that at 13.1µm wavelength.

3.2 Petroleum Jelly

Changes of skin hydration profile resulting from occlusive hydration were studied by applying a very thin coating of petroleum jelly to the dorsal surface of the second finger of the left hand. The third finger of the left hand was used as an untreated control. Petroleum Jelly does not significantly absorb radiation at 2.94 μ m, 6.05 μ m and 13.1 μ m wavelength. It therefore gives access to the stratum corneum for hydration measurement, although its presence on the surface does have an effect on the opto-thermal decay signal through its thermal properties, decreasing the mean opto-thermal decay time (Eq(2)) by up to 20%. Its effects on the determination of surface lifetime and gradient are not known.

The parameters of the control site remained nearly constant during the experiment period, although the scatter of points appears to be larger at early times, and there is a slight upward trend in the surface lifetimes and a slight downward trend in the effective gradients. These changes are attributed to changes in ambient conditions and metabolism.



Figure 4. The results of the effective gradient and surface lifetime at 13.1µm wavelength.

The surface lifetime decreases by about 20% immediately upon application of petroleum jelly. This effect is similar to what was observed when measuring average hydration using Eq(2), and is attributable to changes of heat flow in the presence of the petroleum jelly.

The 13.1µm measurements show a continued decrease during the next half hour, presumably because of increasing hydration. The measurements at 6.05µm do not show this effect, the surface lifetime remaining

effectively constant after the initial application of the petroleum jelly. This finding is surprising. Changes of hydration within the depth probed by these measurements undoubtedly occur, but this measurements appears to be insensitive to them.



Figure 5. The results of the effective gradient and surface lifetime at 6.05µm wavelength.

The decrease in effective gradient immediately upon application of the petroleum jelly mirrors the decrease of surface lifetime. This does not mean that the hydration gradient itself has changes - these changes reflect the changed heat flow in the presence of the petroleum jelly. In the case of the measurements at 13.1 µm, the effective gradient becomes too small to be measured by this technique. At 6.05µm wavelength, the effective gradient in the absence of petroleum jelly is an order of magnitude larger than at 13.1µm wavelength. An initial decrease by a factor of about two occurs, but the gradient remains finite and measurable thereafter. The slow decrease thereafter is mirrored by a similar decrease at the control site and is probably caused by environmental or metabolic factors, rather than hydration changes.

3.3 Dimethyl Sulphoxide (DMSO)

A small quantity of DMSO was applied to the ventral surface of the second finger, with the third finger used as the control site. Measurements were made within two minutes of application, using interference filters of centre wavelengths 13.1 μ m and 9.5 μ m. The reason selecting these two wavelength is because water absorbs strongly at 13.1 μ m, DMSO at 9.5 μ m. The opto-thermal decay times of untreated skin, and therefore the opacity, is almost the same at these two wavelengths.

The surface lifetime of the control site remained nearly constant during the experiments. The gradient of water concentration (13.1µm wavelength) was generally lower than during the experiments with petroleum jelly, with large fluctuations. At 9.5µm wavelength, the gradient was lower still, with even larger fluctuations. The reasons for the large fluctuations are not clear at present. They may be simply be a manifestation of a lower sensitivity of the technique to small gradients.



Figure 6. The results of the effective gradient and surface lifetime at 13.1µm wavelength.

The changes of surface lifetime of the treated sites follow the same pattern as the opto-thermal decay times calculated with Eq(2) and already reported ¹². The large increase at 13.1 μ m immediately after application is caused by the presence of DMSO. This is followed by dehydration in the first half hour or so, with hydration recovery thereafter. The gradient measurements confirm this. The gradient remains effectively zero during the first period as the DMSO dissolves the water in the stratum corneum. Once it has disappeared into the skin, the hydration gradient recovers to that of normal skin during the next hour or so.

The pattern of the 9.5 μ m wavelength data is more complicated. The initial decrease of surface lifetime can be attributed to the increase in effective **b** due to the presence of a thin layer of DMSO on the skin surface. The subsequent recovery overshoots the normal skin response. We think this is because DMSO dehydrates the skin, both by the increased trans-epidermal water loss resulting from the disruption of stratum corneum integrity, and by a solvation process, where DMSO takes water with it, as it is absorbed into the skin. By the time the peak is reached, the DMSO has effectively disappeared from the stratum

corneum, leaving it dehydrated. The effective gradient initially falls to zero, indicating the presence of a layer of DMSO on the surface. It recovers to its original value in about the same time it takes for the surface lifetime to recover and overshoot its initial value. The gradient in this case gives a measure of the time taken for the surface film to disappear.



Figure 7. The analysed results of the effective gradient and surface lifetime at 9.5µm wavelength.

4. CONCLUSIONS

This work shows the OTTER can be used to study the hydration profile within the stratum corneum *invivo*. By exploiting the spectral properties, OTTER can be made sensitive changes of hydration caused by the presence of topically applied substances.

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6. REFERENCES

- 1. R.O. Potts, "Stratum Corneum hydration: Experimental techniques and interpretations of results", *J. Soc. Cosmet.Chem.*, <u>37</u>, 9-33, 1986.
- 2. J.L. Leveque and J.de Regal, "Impedance methods for studying skin moisturization", J. Soc. Cosmet.Chem., <u>34</u>, 419-428, 1983.
- 3. S.L. Jacques, "Water content and concentration profile study", PhD. Thesis, 1984.
- 4. B. Idson, "In-vivo measurement of transepidermal water loss", J. Soc. Cosmet.Chem., 29, 573-580, 1978.
- 5. R.O. Potts, "*In-vivo* measurement of water content of the stratum corneum using infrared spectroscopy: A review", *Cosmetics and Toiletries.*, **100**, 27-31, 1985.
- 6. I. Simon, A.G. Emslie, C.M. Apt, I.H. Blank, R.R. Anderson, "Determination of *in-vivo* water concentration profile in human stratum corneum by a photoacoustic method", *IEEE Transactions on Biomedical Engineering*. **BME-26**, 187-195, 1979.
- 7. J.C. Murphy, L.C. Aamodt, "Photothermal Spectroscopy Using Optical Beam Probing: The Mirage Effect", J. Appl. Phys., <u>51</u>, No. 9, 4580-4588, 1980.
- 8. R.M.S. Bindra, R.E. Imhof, A. Mochan and G.M. Eccleston, "Opto-Thermal Technique for *In-vivo* Stratum Corneum Hydration Measurement", *J. De. Physique*, <u>4</u>(C7), pp. 465-468, 1994.
- 9. I.H. Blank, J. Moloney, A.G. Emslie, I. Simon C. Apt., "The diffusion of water across the stratum corneum as a function of its water content", *J. Invest. Dermatol.*, <u>82</u>, 188-194, 1984.
- R.E. Imhof, B. Zhang and D.J.S. Birch, "Photothermal Radiometry for NDE", Progress in Photothermal and Photoacoustic Science and Technology", Ed. A. Mandelis, Vol. II, pp.185-236, PTR Prentice Hall, Englewood Cliffs (USA), 1994.
- 11. R.E. Imhof, A.D. McKendrick and P. Xiao, "Thermal emission decay Fourier transform infrared spectroscopy", *Rev. Sci. Instrum.*, <u>66</u>, No. 11, 5203-5213, 1995.
- R.M.S. Bindra, R.E. Imhof, P. Xiao and J.J. Andrew, "Opto-Thermal skin measurement in the presence of topically applied substances", *SPIE Proc.*, <u>2395</u>, 566-575, 1995.