shorted electrodes to arc lengths of several centimeters. Rapid fluctuations of current that are so often encountered when arcing certain types of samples are eliminated by this regulator.

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High-Sensitivity Attenuated Total-Reflection Spectroscopy

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Spectrophotometric analysis by attenuated total reflection was originally developed by Fahrenfort[1] to utilize its low equivalent penetration of the light beam and, therefore, low sensitivity for the study of highly absorbent samples. Nearly simultaneously, Harrick[2] proposed the method for the study of surfaces because of the low real penetration of the beam. Here sensitivity is at a premium, and in spite of the use of multiple-reflection techniques,[3–8] it remained barely adequate for many cases.[9,10] A considerable increase in the sensitivity of attenuated total-reflection spectroscopy (ATR) would not only resolve this problem but would make the technique useful in microanalysis because of the very low sample thickness required.

The fundamental equations of ATR are studied here in the form of approximate solutions for weakly absorbing samples, and the optimization of the various parameters is discussed.

If a beam of light falls on an interphase between a nonabsorbing medium (the optical system) of index n_1 and an absorbing medium (the sample) of complex index $n'=n_2(1-iK)$ with an angle of incidence β, "total" reflection will take place whenever

$$G=\sin^2\beta-N^2(1-K^2)\geq 0, \tag{1}$$

where $N=n_2/n'$. The absorptivity, as used here, can be expressed as a function of the absorption in cm^{-1}, E, giving

$$K=(2.303\lambda/4\pi n_2)E. \tag{2}$$

The calculation of the attenuation is best made by the generalized Fresnel equations, since the quantum mechanical treatment of ATR (by analogy with the tunnel effect) is extremely complex. These equations give the reflectances for light polarized perpendicularly (R_s) or parallel (R_p) to the plane of incidence as

$$R_s=\left|\frac{\cos\beta-(n'^2-\sin^2\beta)^{\frac{1}{2}}}{\cos\beta+(n'^2-\sin^2\beta)^{\frac{1}{2}}}\right|^2, \tag{3}$$

$$R_p=\left|\frac{n'^2\cos\beta-(n'^2-\sin^2\beta)^{\frac{1}{2}}}{n'^2\cos\beta+(n'^2-\sin^2\beta)^{\frac{1}{2}}}\right|^2, \tag{4}$$

$$R=(R_s+R_p)/2. \tag{5}$$

If, for simplicity, we introduce an additional variable a such that

$$a^2=\tfrac{1}{2}[(G^2+4K^2N^4)^{\frac{1}{2}}-G], \tag{6}$$

then these equations reduce to

$$R_s=1-\frac{4a\cos\beta}{2a^2+G+(a+\cos\beta)^2}, \tag{7}$$

and

$$R_p=R_s\left[1-\frac{4a\sin\beta\tan\beta}{2a^2+G+(a+\sin\beta\tan\beta)^2}\right]. \tag{8}$$

These expressions are rather complicated, but extensive simplification is possible for the case of interest. At low values of K, a is approximately equal to $KN^2/\sqrt{G}$ and is very small. Since the attenuation $(1-R)$ is to a large extent controlled by a, it will be necessary to make G as small as possible. Also, to increase sensitivity, a large number, m, of reflections will be used.

Given these conditions, and substituting Eq. 6, the absorbancies for both polarization cases and for unpolarized light will be given by

$$A_s=4mK\sin\beta\tan\beta/2.303\sqrt{G}, \tag{9}$$

$$A_p=4mK/2.303\sqrt{G}\cos\beta, \tag{10}$$

and

$$A=2mK(1+\sin^2\beta)/2.303\sqrt{G}\cos\beta. \tag{11}$$

The relation A_s/A_p (Ref. 7) is here seen to equal $\sin^2\beta$.

At first sight, A may be thought to increase indefinitely with increasing m. However, two factors restrict increasing m. The first is the nonabsorptive energy loss due to bulk absorption in the optical system (usually negligible) and to reflection losses caused by surface imperfections. If these reflection losses are of the same order of magnitude as the attenuation by absorption, any increase in m will magnify both sample absorption and background absorption. Since background absorption is usually constant, it can be compensated in the measuring system as long as the remaining energy is adequate for absorption attenuation measurements. Thus, m would be a function of the available energy. This cannot be increased indefinitely owing to heating effects. The optical system, to yield large values of m, must be small in at least one dimension (the normal to the interphase) and, therefore, be of small mass and thermal capacity. Even slight heating will produce index changes that alter G significantly and must be avoided. This favors the use of spectrophotometers where the sample compartment receives dispersed light.

By extreme care, it is possible to reduce the nonabsorptive energy loss to levels where this first factor is no longer the controlling one; then m is controlled by the size and complexity of the optics. The cost of the materials, the accuracy with which they must be worked, and the surface-quality problem make this controlling factor definitely nontrivial.

If the dimensions of the system are L in the direction of propagation of the light beam and l in the normal to the interphase, then

$$m = L/l \tan\beta. \tag{12}$$

Sensitivity improves as G decreases; for small G, using the approximations made previously, we have

$$G = (\beta - \beta_L) \sin 2\beta. \tag{13}$$

When $(\beta - \beta_L)$ is very small, the existence of a small spread, $\Delta\beta$, in the incidence angle become appreciable. If the energy of the beam is uniformly distributed through the interval $\beta \cdots \beta - \Delta\beta$ an average for $(1/\sqrt{G})$ may be used:

$$(1/\sqrt{G})_{\text{av}} = \frac{\sqrt{2}}{(\sin\beta \cos\beta)^{\frac{1}{2}} (\beta - \beta_L)^{\frac{1}{2}} [1 + (1 - \Delta\beta/\beta - \beta_L)^{\frac{1}{2}}]}. \tag{14}$$

To maintain "total" reflection $(\beta - \beta_L)$ must exceed $\Delta\beta$. Because the error in setting β can be made very small, the closeness of approach will depend mainly on the presence of small fluctuations in operating conditions. The safety margin used may be expressed by the factor

$$S = (\beta - \beta_L)/\Delta\beta. \tag{15}$$

Two components make up $\Delta\beta$: a constant amount $\Delta\beta_1$, due to imperfect collimation of the beam and to variations in N, and a cumulative one $\Delta\beta_2$ dependent on m, due to geometrical imperfections in the optical system that change β by a small amount (α radians) at each reflection. If $p = \Delta\beta_1/\Delta\beta_2$, then

$$\beta - \beta_L = S(L\alpha/l \tan\beta)(1 + p). \tag{16}$$

If Eqs. 2 and 12–16 are introduced into Eq. 11 and the approximation $\beta = \text{arc} \sin N$ (valid for small values of K and G) is used, we have

$$A = 0.224 \left(\frac{L}{l}\right)^{\frac{1}{2}} \left(\frac{1}{\alpha^{\frac{1}{2}}}\right) (\sqrt{S} - (S-1)^{\frac{1}{2}}) \times \left(\frac{1}{(1+p)^{\frac{1}{2}}}\right) \left(\frac{1+N^2}{N(1-N^2)^{\frac{1}{2}}}\right) \left(\frac{\lambda}{n_2} E\right) \tag{17}$$

The factor containing N would be $2N/(1-N^2)^{\frac{1}{2}}$ and $2/N(1-N^2)^{\frac{1}{2}}$ for A_s and A_p, respectively.

Examination of Eq. 17 shows that, beyond a certain point, increasing the length-to-thickness ratio of the optics is not a very efficient way to increase A. In fact, if there is any increase in the geometrical imperfections of the system as L/l is increased, no improvement at all is obtained. It must be remembered also that any bending of the system increases $\Delta\beta_1$.

A very effective way of increasing A is to reduce α, S, and p. To achieve a considerable increase in A, these three parameters must be very small; the system will be very sensitive to any changes in them. To achieve high accuracy would be difficult under any conditions more stringent than constant wavelength monitoring. But even this would be useful (for example, in detectors for gas chromatography). And, on the other hand, most spectrometric methods for ultramicro quantities are not noted for their accuracies.

The factor containing N varies according to Table I. The fourth column of Table I gives the increase in sensitivity available when using a beam polarized parallel to the plane of incidence. Numerous difficulties appear here and the gains obtained are not very large.

For good sensitivity the index of the optics should be chosen so that the factors in N attain the highest possible values for the average sample index. Fine adjustment of G is then made by changing β a small amount. For widely varying sample indexes, several optical systems of different materials should be used. When increasing β to obtain higher absorptions, it should be be remembered that, at high values of β, the losses from surface scattering increase disproportionately.

The optimization of the factor $(\lambda/n_2)E$ is hampered

Table I. Values for N.

N	$\beta = \text{arc} \sin N$	$\frac{2}{N(1-N^2)^{\frac{1}{2}}}$	$\frac{2N}{(1-N^2)^{\frac{1}{2}}}$	$\frac{1+N^2}{N(1-N^2)^{\frac{1}{2}}}$	$\frac{2}{1+N^2}$
0.173 65	10°	11.695	0.353	6.024	1.941
0.342 02	20°	6.223	0.728	3.476	1.790
0.500 00	30°	4.619	1.155	2.887	1.600
0.584 01	35°44′	4.219	1.439	2.828	1.492
0.632 79	40°	4.062	1.678	2.870	1.415
0.707 11	45°	4.000	2.000	3.000	1.333
0.766 04	50°	4.062	2.384	3.223	1.260
0.866 03	60°	4.619	3.464	4.041	1.143
0.939 69	70°	6.223	5.495	5.859	1.062
0.984 81	80°	11.695	11.343	11.519	1.015

Table II. Eaxmples of application of suggested calculations.

Optical material	Case 1 Fused silica	Case 2 Synthetic fluor-phlogophite
Optical material index	1.47	1.6
Sample index	1.37	1.5
N	0.9397	0.9375
Approx. β (deg)	70	70.
λ (mμ)	650	250.
S	4	1.2
α	10^{-6} (0,2″)	5×10^{-6}(1″)
L (cm)	10	1
H (mm)	10	1
l (μ)	100	20
p	3	8
$\Delta\beta$ (min)	4	28
A/E (mm)	2.65	5.42
$d_{10}-3$ (μ)	4.2	1.8
A/W ϵ	213 000	10 600 000

because of the restricted choice of λ, n_2, and E for any particular sample. When working with pure or concentrated condensed phases, the whole factor must be optimized. In dilute solution, n_2 is controlled by the solvent index, which should be as low as possible. In gases, the nearly ideal case of $n_2 \approx 1$ exists. In both cases, only λE needs optimization. When making the necessary choices, it should be remembered that higher values of E in the ultraviolet and visible regions often outweigh the higher λ of the infrared. On the other hand, the smaller λ, the higher the requirements on surface quality become.

If Eq. 17 is rewritten by passing E to the left-hand side, we obtain the sensitivity of the measurements in terms of sample absorption intensity. This has the dimension of length, and is often called the "equivalent penetration" of the beam. If E in the original formula is replaced by ϵ, the absorptivity, the sensitivity in terms of sample concentration is obtained.

The sample thickness of second medium depends on the real penetration of the beam. At a distance d from the interphase, the intensity of the beam in the second medium is given by

$$I_d = I_0 \epsilon^{-[(4\pi\sqrt{G})/N(\lambda/n_2)]\,d}, \tag{18}$$

according to electromagnetic theory.

If we take as the sampled thickness that value of d that reduces I_d a thousandfold from its initial value, and substitute Eqs. 12–16 in it, we obtain

$$d_{10^{-3}} = 0.78(L/l)^{-\frac{1}{2}}(1/\alpha^{\frac{1}{2}})[S^{\frac{1}{2}} - (S-1)^{\frac{1}{2}}] \times[1/(1+p)^{\frac{1}{2}}][N/(1-N^2)^{\frac{1}{2}}](\lambda/n_2). \tag{19}$$

For smaller values of d, a correction factor of

$$1 - \epsilon^{-[(4\pi\sqrt{G})/N(\lambda/n_2)]\,d} \tag{20}$$

must be applied to Eq. 17.

The necessary amount of sample in moles may be calculated for an assumed optical system (consisting of a long thin plate between whose faces, coated with sample, the light beam reflects back and forth) by using the equation

$$W = 0.002\,HL[M]d, \tag{21}$$

where H is the width of the plate and $[M]$ is the molarity of the sample. By studying Eqs. 20 and 21, it can be seen that, at extremely low values of d (of the order of a monomolecular layer), the absolute sensitivity A/W of the system tends to a maximum value

$$A/W = (10^3/Hl)\,[(1+N^2)/N^2]\,\epsilon. \tag{22}$$

Although Eq. 22 does not contain L, a value of it that will assume several reflections is implicitly present in the previous approximations.

A numerical example might be useful. Two cases are given in Table II—one representing the present "state of the art," and one representing future possibilities near at hand.

If, in the second example, the sample is assumed to have an absorptivity of 10^5, about 9.4×10^{-13} moles of it will give absorbancy of 1. Detection limits may be regarded as being at least two orders of magnitude lower than this, and amount to less than 10^{10} molecules, or about 10^{-4} of a monolayer.

These sensitivities are high even when compared to microspectrophotometry. But in microspectrophotometry all sample dimensions decrease together, so that, for high sensitivity, thin samples of high absorption intensity are needed. In ATR, "equivalent penetration" is easy to modify, and at its usual values even weakly absorbing samples may be measured. In a more general way, in going from microspectrophotometry to ATR, small sample area is sacrificed for small sample thickness and/or absorption intensity.

If it became possible to use fiber-optical techniques in ATR with the same degree of optimization of parameters as described here, a considerable increase in sensitivity would be possible.

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