Chemiluminescence Spectroscopy

Introduction

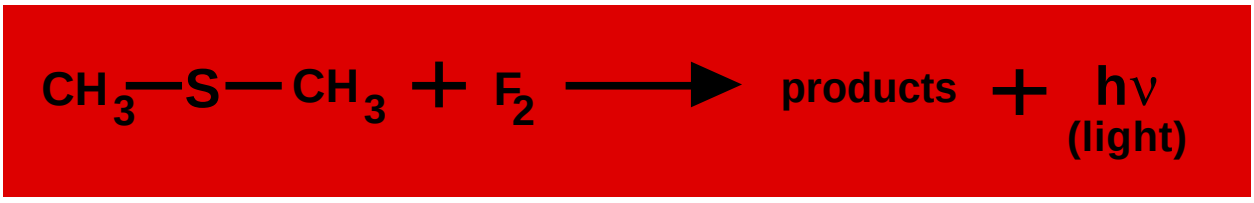
Chemiluminescence, like atomic emission spectroscopy (AES), uses quantitative measurements of the optical emission from excited chemical species to determine analyte concentration; however, unlike AES, chemiluminescence is usually emission from energized **molecules** instead of simply excited atoms. The bands of light determined by this technique emanate from molecular emissions and are therefore broader and more complex then bands originating from atomic spectra. Furthermore, chemiluminescence can take place in either the solution or gas phase, whereas AES is almost strictly as gas phase phenomenon.

Though liquid phase chemiluminescence plays a significant role in laboratories using this analytical technique (often in conjunction with liquid chromatography), we will concentrate on gas phase chemiluminescence reactions since the instrumental components are somewhat simpler. These detectors are also often used as detectors for gas chromatography.

Like fluorescence spectroscopy, chemiluminescence's strength lies in the detection of electromagnetic radiation produced in a system with very low background. And on top of this, because the energy necessary to excite the analytes to higher electronic, vibrational, and rotational states (from which they can decay be emission) **does not** come from an external light source like a laser or lamp, the problem of excitation source scattering is completely avoided. The major limitation to the detection limits achievable by chemiluminescence involves the dark current of the photomultiplier (PMT) necessary to detect the analyte light emissions.

If the excitation energy for analytes in chemiluminescence doesn't come from a source lamp or laser, where does it come from? The energy is produced by a chemical reaction of the analyte and a reagent. An example of a reaction of this sort is shown below:

A chemiluminescence reaction:



In gas phase chemiluminescence, the light emission (represented as h–Planck's constant times ν–the light's frequency) is produced by the reaction of an analyte (dimethyl sulfide in the above example) and a strongly oxidizing reagent gas such

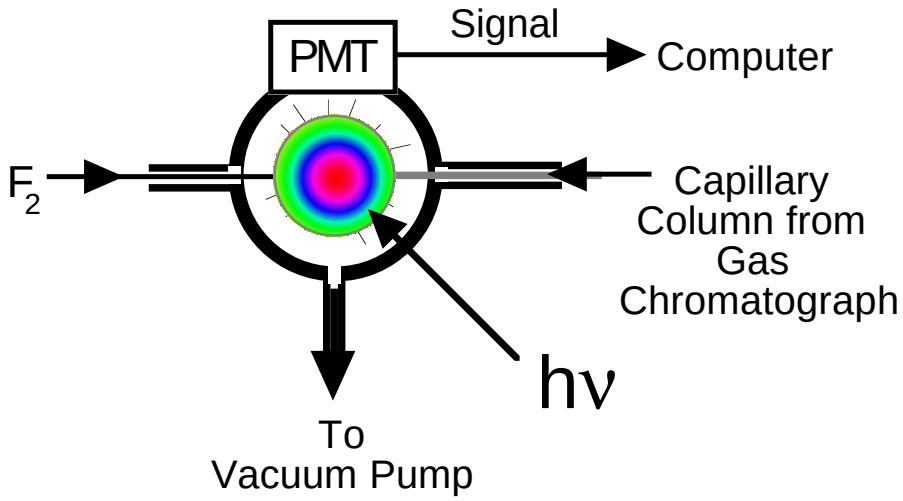
as fluorine (in the example above) or ozone, for instance. The reaction occurs on a time scale such that the production of light is essentially instantaneous; therefore, most analytical systems simply mix analytes and the reagent in a small volume chamber directly in front of a PMT. If the analytes are eluting from a gas chromatographic column then the end of the column is often fed directly into the reaction chamber itself. Since as much of the energy released by the reaction should (in the analyst's eye) be used to excite as many of the analyte molecules as possible, loss of energy via gas phase collisions is undesirable, and therefore a final consideration is that the gas pressure in the reaction chamber be maintained at a low pressure (~ 1 torr) by a vacuum pump in order to minimize the effects of collisional deactivation.

It must be stated that the ambiguous specification of "products" in the above reaction is often necessary because of the nature and complexity of the reaction. In some reactions, the chemiluminescent emitters are relatively well known. In the above reaction the major emitter is electronically and vibrationally excited HF; however, in the same reaction, other emitters have been determined whose identities are not known and these also contribute to the total light detected by the PMT.

To the analytical chemist the ambiguity about the actual products in the reaction is, in most case, not important. All the analyst cares about is the sensitivity of the instrument (read detection limits for target analytes), its selectivity-that is, response for an analyte as compared to an interfering compound, and the linear range of response.

Here is a schematic of the components necessary for a gas phase chemiluminescence detector interfaced to a capillary gas chromatograph.

Schematic of a GC chemiluminescence detector:



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