

LASER DETECTION OF TRACE ELEMENTS

Several elements are present in the environment (physical, biological or geological) in extremely small concentrations, measured in parts per million (ppm), parts per billion (ppb) or even less. These are referred to as the trace elements. Some of the trace elements have a profound influence on their environment totally out of proportion to their meager abundances, and some by their presence can provide valuable information about the environment. Therefore, considerable efforts have been put over the last few decades to develop more sensitive techniques for detecting trace concentration of elements in different environments. This has led to a remarkable progress and it is now possible, with the techniques routinely used in laboratory (like chromatography, spectrometry, neutron activation analysis etc.) to detect most elements to a level of 100 ppb. Still better detection sensitivity is, however, required for many important applications, such as, measurement of trace impurities in semiconductor industry, carcinogens / pollutants in environment / human system, search of useful minerals etc. Further, a fuller exploitation of many applications, notably the latter two, demand capability of remote detection over large areas.

Lasers, due to their high spectral brightness are particularly suited for remote detection of trace elements over large areas. Indeed, laser based LIDAR (Light Detection and Ranging) technique has been in operation since early seventies. This technique has provided valuable information about the acid rain and the hole in ozone layer. More recently, a number of laser based techniques have been developed to provide detection sensitivity of less than 1 ppt (parts per trillion). The ultimate sensitivity of the laser based techniques has been beautifully demonstrated through detection of a single sodium-like atom crossing the laser beam. Laser based techniques have been used for detecting trace concentration of precious elements in ocean water, of aluminum and other toxic trace elements in human and other living systems, and of rhodium and iridium concentrations to ppt level in geological materials. Interestingly, the later has provided confirmation to the hypothesis that mass extinction of dinosaurs occurred 65 million years ago as a result of a large extra-terrestrial body falling upon the earth.

This article provides a brief outline of the various laser based techniques for trace element detection and the work initiated at CAT in this area.

The simplest laser based approach for detection of an element in a given sample is to measure the absorption of an incident laser beam at a frequency corresponding to a

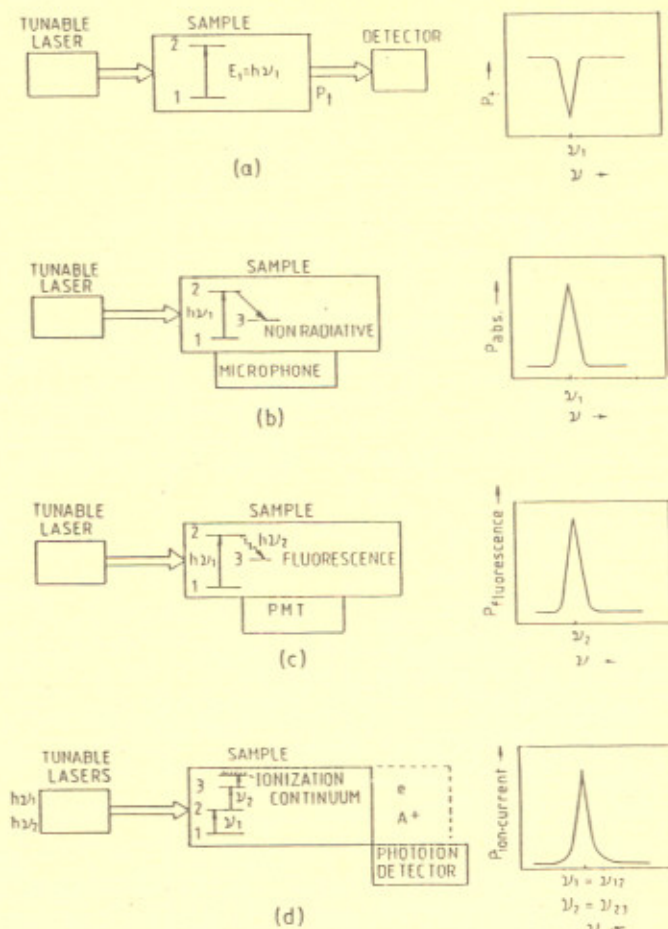


Fig. 1. Basic laser based methods for trace element detection. For samples with adequate absorption, trace concentration can be determined by direct measurement of the transmitted output (Fig. 1a). For weaker absorption, the trace concentration can be determined through measurement of changes in the pressure of the ambient gas (Fig. 1b) or through the measurement of the emitted fluorescence (Fig. 1c). Fig. 1d. shows trace element detection by utilising laser induced selective excitation and photoionization.

characteristic transition. The trace concentration is determined from the changes in the transmitted energy (Fig. 1a). For reliable measurements, the sample absorption should be sufficient to cause a measurable change in transmitted energy, typically greater than 1%. This limits the applicability of this method to cases where strong absorption lines are present for analysis. For weaker absorption, it is often more convenient to directly record the energy absorbed in the sample. This is done primarily in two ways, depending on whether the absorbed energy is

re-radiated in the form of fluorescence or appears as heat due to non-radiative relaxation. In laser photo-acoustic spectroscopy, the changes in the pressure of the ambient gas surrounding the sample are measured with a sensitive microphone (Fig. 1b). In the other method viz. laser fluorescence spectroscopy, the intensity of fluorescence as a function of the laser excitation frequency is measured to identify the element and determine its concentration (fig. 1c). Both of these methods are intrinsically more sensitive compared to absorption, because the latter involves measurement of small changes in intensity against the strong background. An interesting variation to absorption spectroscopy is to place the weakly absorbing sample inside the laser resonator. The strong dependence of the laser output power on weak intracavity absorption has allowed measurement of trace elements to 0.1ppb.

The sensitivity of the fluorescence technique is limited by the relative magnitude of the fluorescence signal and the background radiation reaching the detector. In specially designed cells the background level has been reduced to about 10^{-13} of the incident laser intensity. Further, the fluorescence intensity can be substantially improved in situations where cyclic interaction of the laser beam with the fluorescent species can take place. Thus for example a sodium atom excited by 589nm D1 line, can emit about one thousand photons during its passage through a 5mm diameter laser beam. Since the background signal can be made as low as 2-3 photons, it becomes possible to detect a single sodium atom traversing the laser beam.

Laser induced selective excitation and photo-ionization of atoms and molecules (fig. 1d) is a more versatile technique and can be used for detecting individual atoms of a much wider range of elements. In this technique, two or more tunable laser beams are used for selective, step-wise excitation of the species to a high energy state. The excited species is then ionized by using either an additional laser beam or an external DC electric field when the excited state is close to the ionization limit. A very high photo-ionization selectivity of the desired species is achieved because a number of steps, each with high individual selectivity are involved. With the tunable lasers available, a wide range of elements can be selectively photoionized with a near unity yield. Further, since the detection of the photoionized species can also be performed with a near unity efficiency, the technique is intrinsically very sensitive. In contrast, the sensitivity of the laser induced fluorescence spectroscopy is usually limited by a poor (typically 1%) fluorescence collection efficiency and a low (few tens of percent) photoelectron generation efficiency. The photoionization technique is therefore particularly attractive for detecting atoms in metastable state for which the fluorescence is very weak. Another impor-

tant advantage of the technique is the possibility of extracting the detected species from the mixture by applying external electric and magnetic fields. This can be used for the preparation of ultrapure substances.

An important application of laser fluorescence spectroscopy, particularly relevant to the Department of Atomic Energy, is in the exploration of uranium. For this purpose a laser based uranium analyser has been developed at CAT. This analyser can measure trace concentration of uranium to as low as 0.5 ppb in natural aqueous samples obtained from springs, wells etc. The sample analysis can be performed within a minute and does not require any chemical pre-concentration of the sample.

The basic operating principal of the uranium analyser has been described in CAT Newsletter Dec. 1988. Briefly, the analyser utilises the characteristic fluorescence emitted by the uranyl salts in aqueous solutions when irradiated by UV light. The fluorescence radiation spans the spectral range 450nm to 650nm (fig. 2) and can be measured quantitatively by a suitable photodetector. The most serious interference in direct trace analysis of natural waters by this technique is due to dissolved organic compounds which emit intense blue fluorescence and weak longer wavelength emission (fig. 2). This interference is considerably reduced by using a suitable optical filter and utilising the difference in lifetimes of uranyl fluorescence and that of organic compounds in solution (fig. 3). The fluorescence lifetime of most organic molecules seldom exceed a few tens of ns whereas uranyl ion fluorescence persists for a few tens of μ s. It is pertinent to note that though the spectra of the different uranyl salts are generally similar, the fluorescence yield varies considerably. Therefore, the analytical procedure used with the system involves addition of a buffered inorganic complexing reagent. This helps in calibrating the set-up and also in improving the sensitivity due to an enhanced fluorescence yield.

In the set up developed at CAT (fig. 4), UV source is an indigenously developed compact N_2 laser (28cm x 18cm x 11 cm) operating at 337 nm with peak powers of 50 KW, pulse duration 10 ns and frequency 5 to 10 Hz. The laser uses industrial grade N_2 gas. The use of sealed-off spark-gap as switch reduces the total input power requirement to only 60 W. For field applications, the system can, therefore, be run on any commercial uninterrupted power supply working on an automobile battery.

The fluorescence light is detected by a PMT (photomultiplier tube) which is switched on for 40 to 60 μ s after a delay of 15 to 20 μ s from the onset of N_2 laser pulse. This is achieved by applying an electrical pulse to one of the dynodes of PMT. Each output fluorescence pulse is

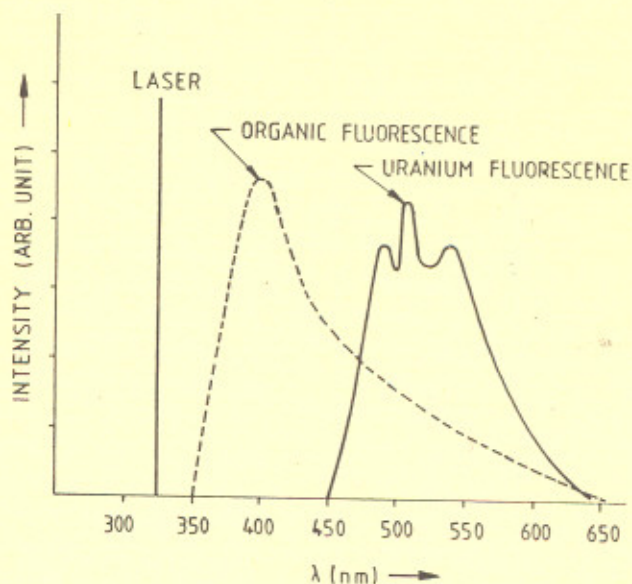


Fig. 2. Solid curve shows the N_2 laser excited fluorescence spectra of Uranyl salts in aqueous solution. The fluorescence spectra of organic compounds present in the aqueous solution is shown by the dotted curve.

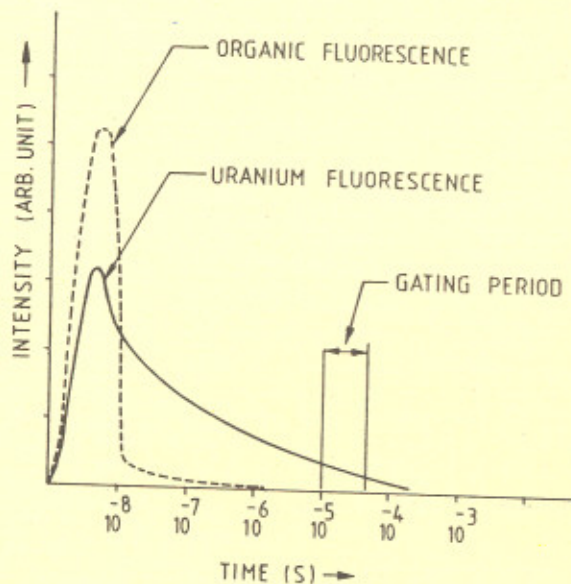


Fig. 3. Temporal response of fluorescence from uranyl salts and organic compounds. The required gating period for the PMT to reduce interference from the organic fluorescence is also indicated.

integrated, digitized and an average value for about 50 pulses is stored on a microprocessor system. To take care of the fluctuations in the the N_2 laser output it is simultaneously monitored by a phototube and the peak power is again averaged for 50 pulses and stored. The signals from the PMT and the phototube are then analysed, and the actual concentration of the sample is displayed on the console. The microprocessor control allows setting up of acceptable upper and lower limits for the laser power and automatic selection of filters (used for attenuating the fluorescence output incident on the PMT) and thus permits measurement over a wide range of concentrations.

The prototype instrument has been used to determine uranium concentration in several water and rock samples provided by chemical laboratory, Atomic Minerals Division, Nagpur. The measurement accuracy of the instrument was found to be comparable to the imported commercial system being used for the purpose.

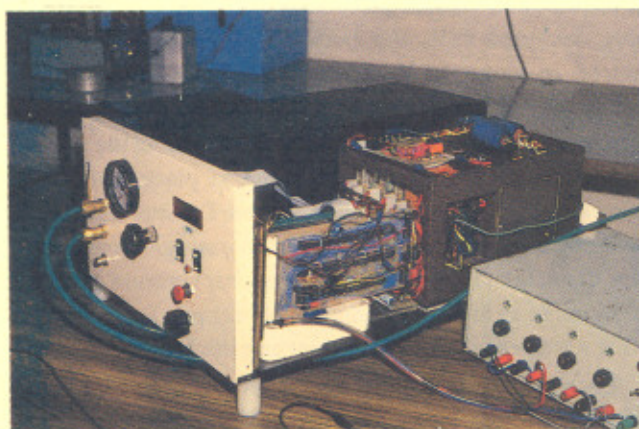


Fig. 4. Laser uranium analyzer developed at CAT. Top photograph shows the inner view of a unit. From left to right are the nitrogen laser system, power supply and the processing cards. The front panel has displays for nitrogen gas pressure, upper and lower limits set for the laser power and the measured uranium concentration. The bottom photograph shows the present prototype model assembled in a standard commercial rack of size 425 X 425 X 145 mm by optimising the various subsystems.