



D I A L

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Detection of Chlorinated Organics and Other Toxic Compounds

There exists a need for a general-purpose, sensitive, real-time detector for toxic compounds of environmental concern. Although there are many laser-based techniques in use for real-time detection of specific molecules, none of them is perfectly general in the sense that each is applicable to a somewhat narrow class of molecules. Laser-induced fluorescence (LIF), for example, is excellent for molecules that fluoresce well but is obviously inapplicable to molecules with low fluorescence quantum-yield. This is especially true for chlorinated aromatic molecules because fast intersystem crossing (ISC) efficiently depletes the laser-prepared excited singlet state via singlet-triplet (spin-orbit) coupling (this is the so-called "heavy atom effect" due to the presence of chlorine). ISC also influences detection schemes based on resonance-enhanced multiphoton ionization (REMPI) by depleting the excited-state on a time-scale faster than the nanosecond-duration of the lasers usually employed, thus lowering the photoionization efficiency. Use of ultrafast lasers could alleviate this problem, but the cost and complexity of such systems would render the method unsuitable for field-deployment. By contrast, the relatively new technique being explored here, cavity ring-down spectroscopy (CRDS), is not plagued by excited-state photophysics and is perfectly general because it is solely absorption-based. It is also superior to other conventional popular techniques such as FTIR spectroscopy because it is more sensitive, and optoacoustic spectroscopy because it can provide absolute absorption cross-section and is thus self-calibrating. It is thus a very promising universal toxic gas detector.

In CRDS, the absorption pathlength of a pulsed laser through an absorbing sample is made very long by trapping the pulse between the mirrors of a high-finesse (low-loss) optical cavity containing the sample. The effective pathlength can be several kilometers, so very small concentrations of chemical species can be detected, limited mainly by the cavity mirror reflectivity and scattering losses. CRDS is more suitable for environmental work than conventional multipass absorption spectroscopy (with a White cell) because long optical pathlengths are more easily attained.

Our experimental setup is shown schematically in Figure 1. Pulsed (nanoseconds) output from a laser is injected into a high-finesse optical cavity containing an absorbing species, and the time-decay of the transmitted light is monitored by a photomultiplier. The cavity is formed by two mirrors of very high reflectivity (preferably $R > 0.999$). The cavity is

enclosed in a stainless cell the ends of which are made vacuum-tight by quartz windows. The mirrors and windows are mounted in flanges that are connected to the rest of the cell by flexible bellows and are held in precision adjustable mounts for optical alignment. In an empty cavity (without the sample), the only loss mechanism is the small transmission of the mirrors and the pulse can be trapped in the cavity for microseconds, making a large number of round-trips. The cavity transmission decays exponentially (curve (a) in Figure 1) with a characteristic $1/e$ decay-constant (the "ring-down" time τ) which is a function of mirror reflectivity and cavity length only. If an absorbing species is present in the cavity, an additional loss mechanism is introduced and the ring-down time τ decrease and the transient signal decays faster (see curve (b) in Figure 1). An analysis of the ring-down waveform can thus yield the absorption cross-section.

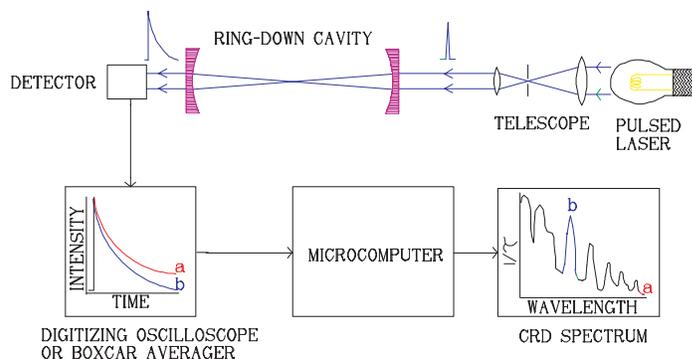


Figure 1. Schematic diagram of the CRDS setup.

In our early feasibility study, described in Ref. 1, we used a somewhat short cavity, relatively cheap and somewhat sub-standard mirrors ($R \sim 0.9803$ - 0.9945), and a fixed-wavelength laser (266 nm) to detect simple chlorinated aromatics (chlorobenzene and 1,2-, 1,3-, and 1,4-dichlorobenzenes). We found that detection of these volatile organics in the ppm range is straightforward. We can improve the sensitivity by incorporating changes to the experimental setup. In the above experiments, the absorption pathlength was only 0.024-0.086 km (for $t = \tau$) because of the short cavity length and substandard mirrors. With better ultraviolet mirrors (higher R) and a longer cavity (>50 cm), an effective pathlength of >2.5 km is possible. Significant additional improvement is possible by using a tunable ultraviolet laser instead of the fixed wavelength (266 nm) used in the above feasibility work (some of these improve-

ments have been already incorporated in more recent work in progress). Sensitivity in the ppb range can be attained in suitable cases. Sensitivity in the ppt range (or less) may be attainable by preconcentration (for a few minutes) of environmental samples prior to analysis.

The most significant aspect of this work is the ease with which chlorinated aromatics can be detected by CRDS. In addition, the sensitivity is unaffected by the extent and site of chlorination. In this respect, CRDS is superior to other laser-based methods that are influenced by excited-state photophysics. Techniques such as LIF and REMPI are influenced by ISC, as mentioned previously. In addition, this increases with increasing chlorine content, thus requiring extensive calibration even in cases where these techniques "work."

CRDS will also be useful for detecting other chlorinated VOCs, and for distinguishing between different aromatics because the absorption wavelengths are quite sensitive to the number, type and position of substituents on the phenyl ring (i.e., the molecular structure). Consequently, it is also possible to characterize a mixture of VOCs, provided their spectroscopy is understood. CRDS will also be suitable for detecting larger chlorinated aromatics of environmental concern, such as dioxins. These compounds are generated as unwanted by-products of high-temperature processes such as waste incineration and are among the most toxic man-made chemicals. The need for a detector for this class of molecules is thus quite obvious. Successful application of CRDS to dioxin detection, however, will be challenging because these semi-volatile organics have low vapor pressures and the detection limits specified by the EPA for verifying compliance are stringent. Preconcentration (for a few

minutes) can alleviate this problem. We also note that simpler (monocyclic) chlorinated volatile aromatics, such as the chlorobenzenes mentioned above and chlorophenols, have been suggested as environmental "surrogates" for the semivolatile dioxins because they are easier to detect as they are present in larger concentrations, and there is some correlation between their concentration and dioxin concentration in incinerator emission. Thus, their detection will provide an "early warning" for the presence of chlorinated dioxins. Be that as it may, we feel that a useful dioxin detector, based either on direct dioxin-detection or detection of dioxin-surrogates, is within reach.

In addition to chlorinated organics mentioned above, CRDS can be used to detect other, smaller pollutants such as NO₂, SO₂, etc. (see Ref. 1 for NO₂ detection).

Reference

1. R. Vasudev, A. Usachev and W.R. Dunsford, "Detection of Toxic Compounds by Cavity Ring-Down Spectroscopy," *Environmental Science & Technology*, in press (1999).

Additional information regarding CRDS and other applications may be obtained from:

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