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AN IMPROVED OSCILLOGRAPHIC CAMERA TECHNIQUE FOR
TIME-RESOLVED MASS SPECTROMETER DATA RECORDING*

Facsimile Price \$ 1.10

Microfilm Price \$.80

Available from the
Office of Technical Services
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INTRODUCTION

The application of mass spectrometers to time-resolved studies of chemical and physical processes occurring on the time scale of milliseconds and microseconds has received wide attention in recent years. In part, this is the result of the development of rapid scanning time-of-flight mass spectrometers. Simultaneously, various techniques have been advanced for the extraction, recording, and processing of the rapidly changing mass spectral data.

Figure 1 is a schematic summary of several of these data recording techniques. Shown in the upper left is the typical amplitude vs mass display observed with an oscilloscope output for a Bendix Time-of-Flight Mass Spectrometer. The methods of Damoth¹ and Kendall² for recording amplitude vs time both utilize electron beam intensification and Polaroid film recording.

The revolving drum camera technique consists of the high speed movement of a strip of film vertically past the standard oscilloscope display in order to time-resolve and permanently record successive scope traces of amplitude vs mass. Kistiakowsky and Kydd³ employed this data recording method for the study of gas phase chemical reactions induced by flash photolysis and shock wave. However, low overall photographic sensitivity and time-consuming data reduction have been limiting features. This paper describes several improvements which have been made which now render the drum camera method a means for legible data recording and efficient data reduction.

Desirable features of this oscillographic camera technique for time-resolved mass spectrometer data recording are as follows. First, any and all mass spectral signals occurring within the mass range being displayed by the oscilloscope will be simultaneously recorded on the film strip. This is particularly important for those systems producing intermediate species such as atoms, free radicals, or other molecular fragments, which may be completely absent at both the beginning and end of a transient experiment and which may be unknown to exist prior to the experiment. Second, each trace of the film record carries a baseline for zero amplitude reference which is common to all the masses under observation. Third, absolute mass identification is provided by interpolation between known masses. Fourth, essentially independent coordinate axes are utilized to display amplitude, mass, and time. This minimizes problems of signal overlapping and mass and time resolution.

PHOTOGRAPHIC SENSITIVITY

Factors controlling the effective photographic sensitivity are listed in Table I, along with a numerical estimate of the sensitivity obtained in this work relative to that utilized by Kistiakowsky and Kydd.³ The first two factors, the CRT phosphor and the film emulsion, are conveniently considered together. The combination of a P16 phosphor with Agfa Isopan Record film yields a net loss in sensitivity of approximately a factor of one half in comparison to the combination of a P11 phosphor with Kodak Linagraph Pan film. The shorter persistence, 0.1 μ sec, of the P16 phosphor is required with the overall increased sensitivity provided by the other factors. The vertical motion of the film strip causes image streaking with

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Fig. 1 Schematic summary of three data recording techniques for time-resolved mass spectrometry.

TABLE I. FACTORS CONTROLLING EFFECTIVE PHOTOGRAPHIC SENSITIVITY

ITEM	KISTIAKOWSKY AND KYDD ³	THIS WORK	RELATIVE SENSITIVITY
CRT PHOSPHOR	P11 (30 μ sec, 4550A)	P16 (0.1 μ sec, 3850A)	1/2
FILM	LINAGRAPH PAN (2600) ^a ROYAL-X PAN (6300) AGFA ISOPAN RECORD	AGFA ISOPAN RECORD ROYAL-X PAN (600) AGFA ISOPAN RECORD	
ACCELERATING POTENTIAL	10 kv	28.5 kv 12 vs 24 kv 12 vs 28.5 kv	10 6 8
SWEEP RATE	1 μ sec/cm	1 μ sec/cm 1.0 / 0.1 μ sec/cm	1 3/4
LENS APERTURE	f 3.5	f 2.3	9/4
FILM PROCESSING	—	20 min in Rodinal at 68°F or Sensitized	—

a. Relative CRT - Film Speed, ref. 4.

b. Data on Royal-X Pan film taken from ref. 4.

c. Data on Agfa Isopan Record film obtained in this work.

the longer persistence phosphors. The effect of the increased emulsion speed of the Agfa Isopan Record is appreciated by noting that the relative sensitivity would be one-thirteenth if the Kodak Linagraph Pan were used with the P16 phosphor.⁴ Indirect experiments indicate that Agfa Isopan Record may be faster than Kodak Royal-X Pan at 3850A for this type of data recording by a factor of two; at least, clearer, less noisy negatives are obtained from the Agfa film.

The loss in sensitivity with this phosphor-film combination is regained with a larger effective lens aperture. A Beckman and Whitley Model 364-2 Oscillographic Camera, equipped with a Wollensak f 1.9 Oscillo-Raptar lens, is used. In actual application, the lens system has an effective aperture of f 2.3.

The most significant single factor contributing to the increased trace recording capability is the 28.5 kv accelerating potential on the electron beam of a modified Tektronix Type 517A oscilloscope. Actual experiments have shown, with the P16 phosphor, that by stepping up the potential from 12 kv to 24 kv a gain of a factor of six in sensitivity is achieved; boosting the potential to 28.5 kv raises this to a factor of eight. It is estimated, therefore, that the sensitivity ratio for 28.5 kv vs 10 kv is approximately ten. Variation in the horizontal sweep rate has only a minor effect on the sensitivity over the range of 1.0 to 0.1 μ sec/cm.

The effect of the mode of film processing is significant. Extended development can increase the film speed by a factor of two to ten, depending upon the particular emulsion. Kodak data⁴ indicate that, for Royal-X Pan film exposed to a P16 phosphor, increasing the development time in Kodak D-19 from 4 to 15 minutes increases the film speed by a factor of twenty. In our work, a 20 minute development time was used for both Royal-X Pan in Kodak D-19 and Agfa Isopan Record in Rodinal. We have also tried chemically sensitizing our exposed films prior to development. For the recording of mass spectral signals, we have found no significant net increase in sensitivity. However, the development time could be halved to obtain the same image density.

Overall, it is estimated that a factor of ten increase in photographic sensitivity has been achieved for time-resolved mass spectrometer data recording with a revolving drum oscillographic camera. Reproductions of actual film records which have been obtained with 20 kc pulsed operation of a Bendix TOF Mass Spectrometer are shown in Figs. 2 and 3. Figure 2b demonstrates the recording of mass signals due to only a very few ions per cycle on the average; note that the mass 14, 16, and 18 peaks do not appear in every trace. Figure 3 illustrates film recordings of higher mass species at faster sweep rates, the faster sweeps being used to achieve increased mass separation in the oscilloscope display.

SYNCHRONIZING CIRCUITS

This data recording system has been assembled for the purpose of performing time-resolved chemical kinetics studies of gas phase reactions excited by flash photolysis. Figure 4 illustrates the auxiliary electronic components which have been instrumented to synchronize the flash lamp with the 20 kc pulsed operation of the spectrometer and to provide effective shuttering action for the oscillographic camera. The principle component of the synchronizing circuit, which is a modification of a scheme developed by Schellenbaum,⁵ is a 5696 tetrode thyatron. The shield grid is biased negatively in the stand-by position, which prevents indiscriminate triggering of the thyatron by 20 kc pulses from

Fig. 2 (a) Mass spectrum of H_2O_2 and CO_2 mixture; masses 44, 34, 32, 28, 18, 17, 16, 14, 12, left to right; (b) Mass spectrum of residual air; masses 32, 28, 18, 16, 14, left to right; masses 14-18 appear randomly; 1.0 μ sec/cm sweep.

Fig. 3 (a) Mass spectrum of SF₆; masses 127, 108, 89, left to right; 0.5 μsec/cm sweep; (b) Mass spectrum of Xe isotopes; masses 136, 134, 132, 131, 130, 129, 128, 126, left to right; 0.2 μsec/cm sweep.

Fig. 4 Electronic components and associated waveforms for synchronization of flash photolysis - time-of-flight mass spectrometer apparatus with shuttering action of the data recording oscillographic camera.

the mass spectrometer appearing continuously on the control grid. When the desired drum speed of the oscillographic camera is attained, a Tektronix Type 163 pulse generator is triggered. This produces a positive pulse of duration greater than the 50 μ sec interval between spectrometer pulses and of amplitude sufficient to offset the negative bias on the control grid of the thyatron. The thyatron fires on the next 20 kc trigger pulse, and subsequent stages in the circuit become synchronized to the mass spectrometer. The thyatron remains conducting, serving as a lockout against multiple triggering. The output signal is differentiated, amplified, inverted and applied to a waveform generator, which simultaneously triggers a time delay generator and a variable width pulse generator.

The camera shuttering circuit utilizes a 6AK5 pentode. It conducts the 20 kc spectrometer pulses applied to the control grid only for the duration of the screen grid gating pulse, which is derived from the variable width pulse generator. The width of the gating pulse is adjusted to be equal to or less than one revolution of the camera drum. Thus, the shuttering action is achieved by triggering the horizontal sweep generator of the oscilloscope a selected number of times rather than by a mechanical shutter. The additive finite risetimes associated with the circuits between the thyatron and the pentode cause the first scope trigger pulse (Fig. 4, waveform 8) to be one pulse later in time than the 20 kc pulse which fires the thyatron. Compensation for this 50 μ sec lag may be achieved with the time delay generator.

The principle function of the time delay generator is to delay the firing of the flash lamp for 20 cycles or so, in order to record on film the mass spectral signals prior to the initiation of the reaction. A short duration electromagnetic pickup from the discharge of the flash lamp distorts the output of the mass spectrometer. This interference is illustrated in the fourth and fifth horizontal sweep traces of Fig. 5a. The principal portion of this interference persists for less than 50 μ sec. Therefore, fine adjustments of the time delay generator may be made to position the discharge in a region of the spectrum which does not contain useful information.

FLASH HEATING EXPERIMENT

Data obtained in experiments in which gaseous nitrogen dioxide was flash heated is recorded in Figs. 5 and 6, as an example of the application of the oscillographic camera technique and the associated electronic circuitry to time-resolved mass spectrometer studies. The nitrogen dioxide was subjected to flash heating rather than flash photolysis for these particular experiments, as a result of both the radiation emitted by the flash lamp and the absorption by the gas favoring wavelengths above the decomposition wavelength. The effect of the flash heating was to increase the gas density in the reaction chamber. This is clearly demonstrated, in the film record of Fig. 5, by the increase in the amplitude of the NO^+ (the major ionization fragment of NO_2) signal subsequent to the flash. Figure 6 is composed of data transferred from three films to graphical representation by our data reduction procedures. The lamp was flashed at time zero, after the spectrum of the nitrogen dioxide had been recorded for one millisecond. The time lag between the lamp flash and maxima in the NO_2^+ and NO^+ amplitudes is a result of non-uniform heating of the gas sample followed by gas flow to the sampling orifice of the ionization chamber. The NO^+ to NO_2^+ ratio remains constant, which is what one expects in the absence of any photochemical decomposition.

In as much as quantitative data reduction can be a very time-consuming process, a brief description follows of methods and facilities used to render data reduction from the film records

Fig. 5 Flash heating of NO_2 ; masses 46, 32, 30 (NO-major peak), 28, 16, 14, left to right; top of (b) follows bottom of (a) in time; lamp flashed during fourth trace of (a) causing signal interference; 50 μsec between traces; 1.0 $\mu\text{sec/cm}$ sweep.

Fig. 6 Time-resolved flash heating of nitrogen dioxide at various gas pressures; NO and NO_2 ion signals recorded before and after lamp flash (time zero).

more efficient and accurate. A semi-automatic film reader is employed to read and record on punched cards the mass position and peak amplitude of each mass spectral signal in the time-resolved mass spectrum. The punched cards are sorted automatically according to mass and supplied to a x,y-coordinate plotter which provides amplitude vs time data plots similar to those shown in Fig. 6. The data cards are also available as an information source for numerical computer programs. For example, in chemical kinetics experiments, it may be necessary to reference numerically each measured amplitude to an internal, inert standard substance in order to account for systematic error; or concentration ratios of reactant to product and intermediate to parent may be required to interpret the detailed chemical processes. A specific example of the latter is the NO^+ to NO_2^+ ratio plot of Fig. 6, for which the interpretation has already been cited.

SUMMARY

A revolving drum camera - oscilloscope data display and recording system has been assembled. It provides an effective photographic sensitivity an order of magnitude greater than that previously reported for utilization in time-resolved mass spectrometer analyses of rapidly occurring physical and chemical processes. A gas phase flash heating phenomenon, recorded with a Bendix TOF Mass Spectrometer operating at 20 kc, is cited as an application of the improved data recording system and as an example of time-saving data reduction procedures.

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