

## Real-Time Chemical Analysis of Aerosol Particles

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### Abstract

An application of an ion trap mass spectrometer (ITMS) for real time chemical analysis of airborne microparticles is described. Fragmentation analysis of organic chemicals condensed on a microparticle's surface has been demonstrated using laser induced desorption ionization and MS/MS techniques with ITMS. An on-line atmospheric particle sampling system has been designed and interfaced to the ITMS. A dual particle detector system using optical fibers has been designed and timing electronics have been developed for the particle speed measurements required in order for the desorption laser to intercept the particles.

**Keywords:** aerosols, environmental monitoring, real-time atmospheric sampling, quadruple ion trap, laser desorption mass spectrometry, MS/MS analysis, optical particle detector, velocity measurements.

### 1. Introduction

An important aspect of environmental atmospheric monitoring requires the characterization of airborne microparticles and aerosols. Unfortunately, traditional sample collection and handling techniques are prone to contamination and interference effects that can render an analysis invalid. These problems can be avoided by using real-time atmospheric sampling techniques followed by immediate mass spectrometric analysis. The former is achieved in these experiments via a two stage differential pumping scheme that is attached directly to a commercially available quadruple ion trap mass spectrometer. Particles produced by an external particle generator enter the apparatus and immediately pass through two cw laser/fiberoptic based detectors positioned two centimeters apart. Timing electronics measure the time between detection events, estimate the particles arrival in the center of the ion trap and control the firing of a YAG laser. Ions produced when the UV laser light ablates the particle's surface are stored by the ion trap for mass analysis. Ion trap mass spectrometers have several advantages over conventional time-of-flight instruments. First, they are capable of MS/MS analysis by the collisional dissociation of a stored species. This permits complete chemical characterization of airborne samples. Second, ion traps are small and lend themselves to portable, field oriented applications.

### 2. Laser desorption mass spectrometry in an ion trap

Chemical analysis of individual microparticles using laser desorption mass spectrometry in our ion trap system has been described elsewhere.<sup>1</sup> Briefly, the particles are introduced into the ion trap by a particle hopper or a particle launcher mounted in the vacuum chamber. When a particle

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arrives at the center, a YAG laser (532 nm) desorbs and ionizes the molecules adsorbed on the microparticle surface. The ions are trapped and subsequently mass analyzed using the mass-selective instability mode of operation of the ion trap.<sup>2</sup> A detection limit of 0.7 fm per particle was determined for tetraphenyl-phosphonium bromide (TPPB) adsorbed on 100  $\mu\text{m}$  silicon carbide microparticles.<sup>1</sup> Also, direct isotope ratio measurements of nickel particles with a size of 50  $\mu\text{m}$  has been demonstrated using the same method.<sup>1</sup>

### **3. MS/MS analysis of microparticles**

For the measurements of MS/MS fragmentation, all masses of ions are expelled except the parent ions. These parent ions are vibrated with an additional low RF voltage between the two end cap electrode, resulting in dissociation through collision with buffer gas atoms. The fragmented ions dissociated from the parent ions are again mass analyzed. This additional information, which cannot be obtained with a conventional time-of-flight mass spectrometer, enhances the specificity of a chemical determination.

The measured primary mass spectrum of TPPB laser-desorbed from a SiC microparticle and the fragmentation mass spectrum dissociated from the mass selected parent ions of  $(\text{C}_6\text{H}_5)_4\text{P}^+$  are displayed in Figure 1(a) and (b), respectively. The molecular structure of the TPPB is also illustrated at the of Figure 1(b). While the primary mass spectrum shows a large number of fragmentation peaks and inorganic background peaks with the parent ion peak, the fragmentation mass spectrum exhibit a recognizable fragmentation pattern in which the peaks correspond to the loss of one, two, or three phenyl groups from the parent ions. This measurement may be interpreted by pattern recognition algorithms for chemical determinations. For example, if the fragmentation pattern of an unknown sample demonstrated a similar fragmentation pattern to that in Figure 1(b), then we would know that the sample molecule consists of four phenyl groups surrounding a base block that also may be determined from the fragmentation pattern.

### **4. Real-time Analysis of aerosol particles**

To apply the MS/MS technique to real-time chemical analysis of aerosol particles, an atmospheric particle sampling system and a dual particle detection system were designed and examined with a particle generator that simulates airborne particulates. Figure 2 illustrates the overall systems including the ion trap, particle detector, atmospheric sampling interface and, particle generator.

#### **4.1 Particle generator**

The particle generator consists of a vibrating orifice with 35  $\mu\text{m}$  diameter, a high pressure sample solution container, and a heated drying tube. The sample solution is nebulized through the orifice mounted on a Piezo ceramic vibrator that usually operates at 50 kHz. The sprayed liquid droplets are dried while flying through the warm tube carried by slowly flowing nitrogen into the ion trap sampling interface. Since the size of the liquid droplets is determined by the orifice size, flow rate, and vibrator frequency, the dried salt particle size can be controlled by changing the concentration of the sample solution. Figure 3 shows an SEM microscope picture of microparticles

generated with a solution of 1 g  $\text{-KNO}_3$  in 200 ml of  $\text{H}_2\text{O}$ .

#### 4.2 Atmospheric particle sampling system

The air sample with suspended aerosol particles was injected through a 1.6 mm diameter hole into the first interface region and further expanded through a capillary, 0.5 mm diameter and 25 mm long, into the second interface region in which a 100 mtorr of gas pressure was achieved with a pumping speed of 500 l/min. The particles successively travel through a skimmer into the ion trap where the residual gas pressure was approximately  $10^{-4}$  torr. The ion trap chamber, however, was filled with 1 mtorr of Helium to optimize ion mass measurement. The diameter of the skimmer orifice was 500  $\mu\text{m}$  and the ion trap pumping speed was 80 l/s.

#### 4.3 Fiberoptics particle detector

An Argon ion laser beam was introduced through an optical fiber to illuminate the particle beam path right below the skimmer and scattered light was collected with another fiber optic that leads to a photomultiplier tube outside the vacuum chamber. Another identical detector system was located 19.2 mm below the first detector along the beam path. The particle detection pulses from both PMTs were sent to the timing electronics as shown in Figure 4. The up-counter chip starts counting the clock pulses by the first detector signal. When the second PMT detects the particle it stops up-counting and simultaneously down counter chip starts counting down from the previously counted number to zero, ending with an output pulse. The up and down counters count the same number of pulses, however, the repetition rates of the clock pulses provided to the both counters are set to the ratio of L2 to L1, the distance from the second detector to the center of the ion trap and the distance between the two detectors, respectively, so that the down counter generates a trigger pulse at the particle arrival time at the center of the ion trap. Figure 5 shows the particle signals coincidentally detected by the first and the second PMTs. The speed of the particles was estimated by dividing the detector distance by this time interval. The measured speed distribution of the  $\text{KNO}_3$  particles with a diameter of 15  $\mu\text{m}$  injected from the air to the vacuum chamber is illustrated in Figure 6.

### 5. Summary and conclusion

The demonstrated MS/MS measurements of the organic chemicals desorbed from a microparticles surface indicates that chemical composition of aerosol particles can be completely analyzed directly from the air without any sample manipulation. The fiberoptic particle counter enables one to detect the injected particles from the air and to trigger the desorption laser to intercept the particle. The speed distribution of the particles with a size of 15  $\mu\text{m}$  was measured to be 90 - 140 m/s. Detailed information about the particle transmission efficiency, minimum detectable particle size, ratio of neutral to charged particles, and mass spectroscopic investigation of various aerosol particles will be available in the near future.

## 6. Acknowledgement

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## 7. References

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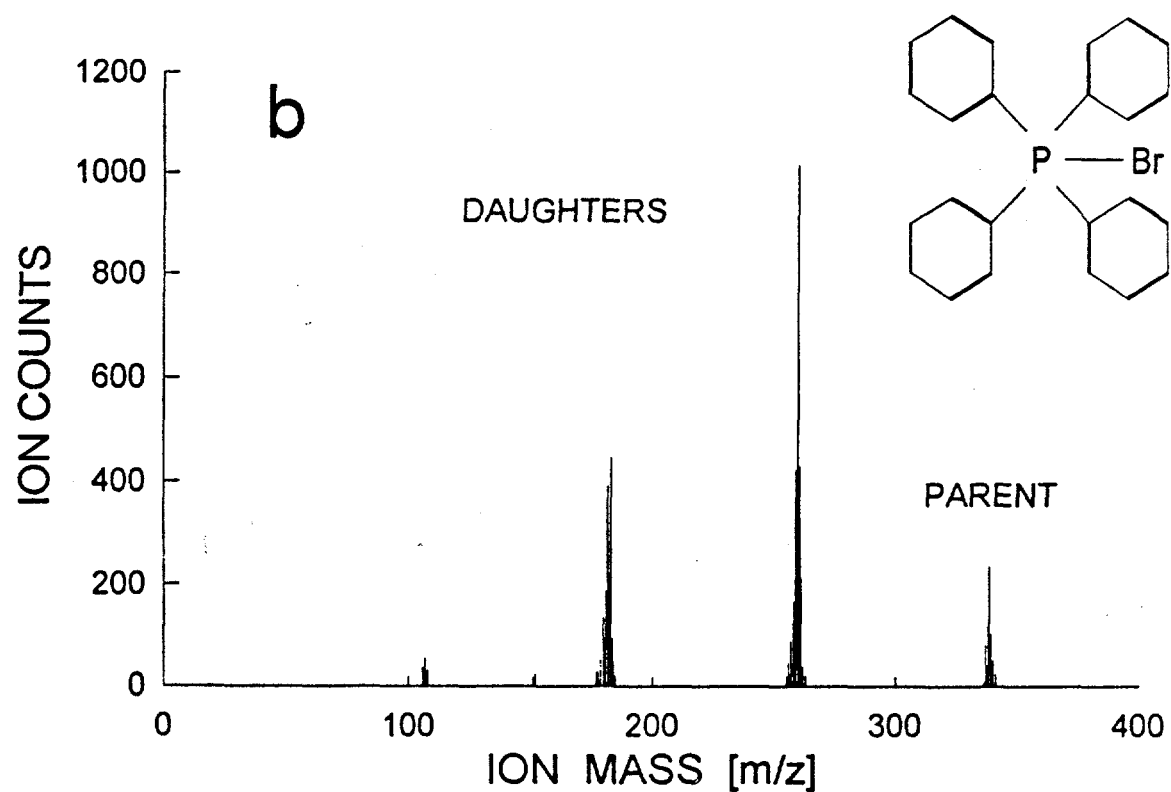
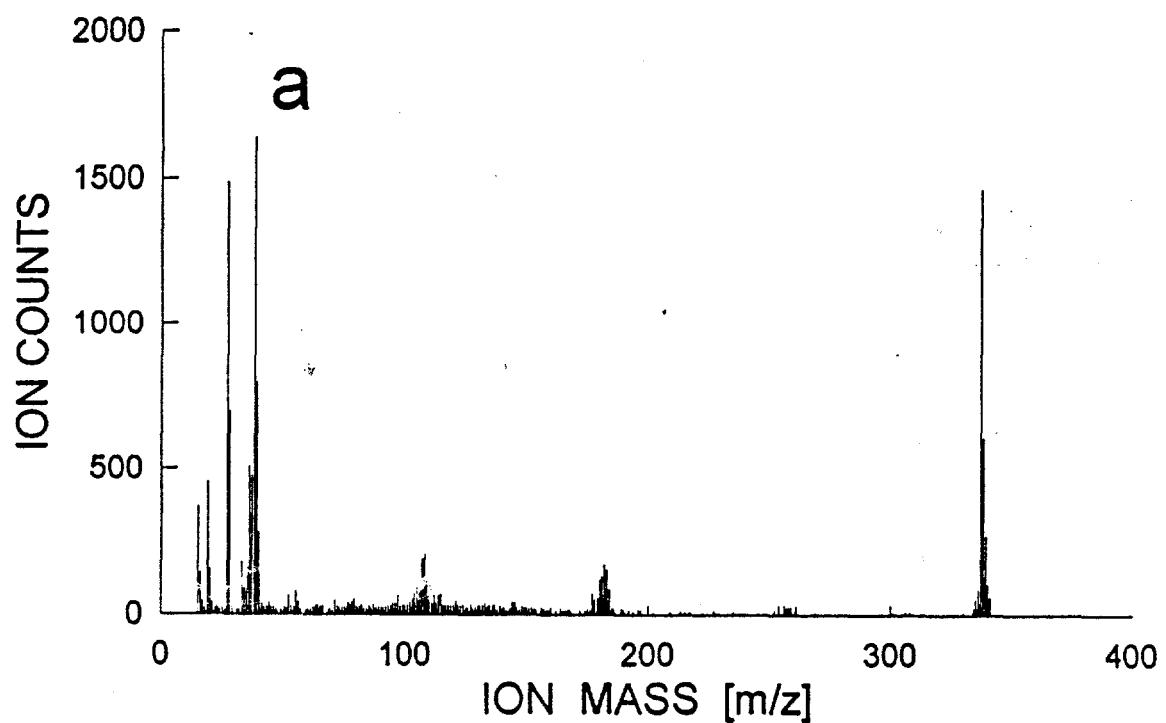


Figure 1. (a) Primary mass spectrum of TPPB laser-desorbed from the surface of a SiC microparticle. (b) Secondary mass spectrum of fragments dissociated from the parent ions of TPPB.

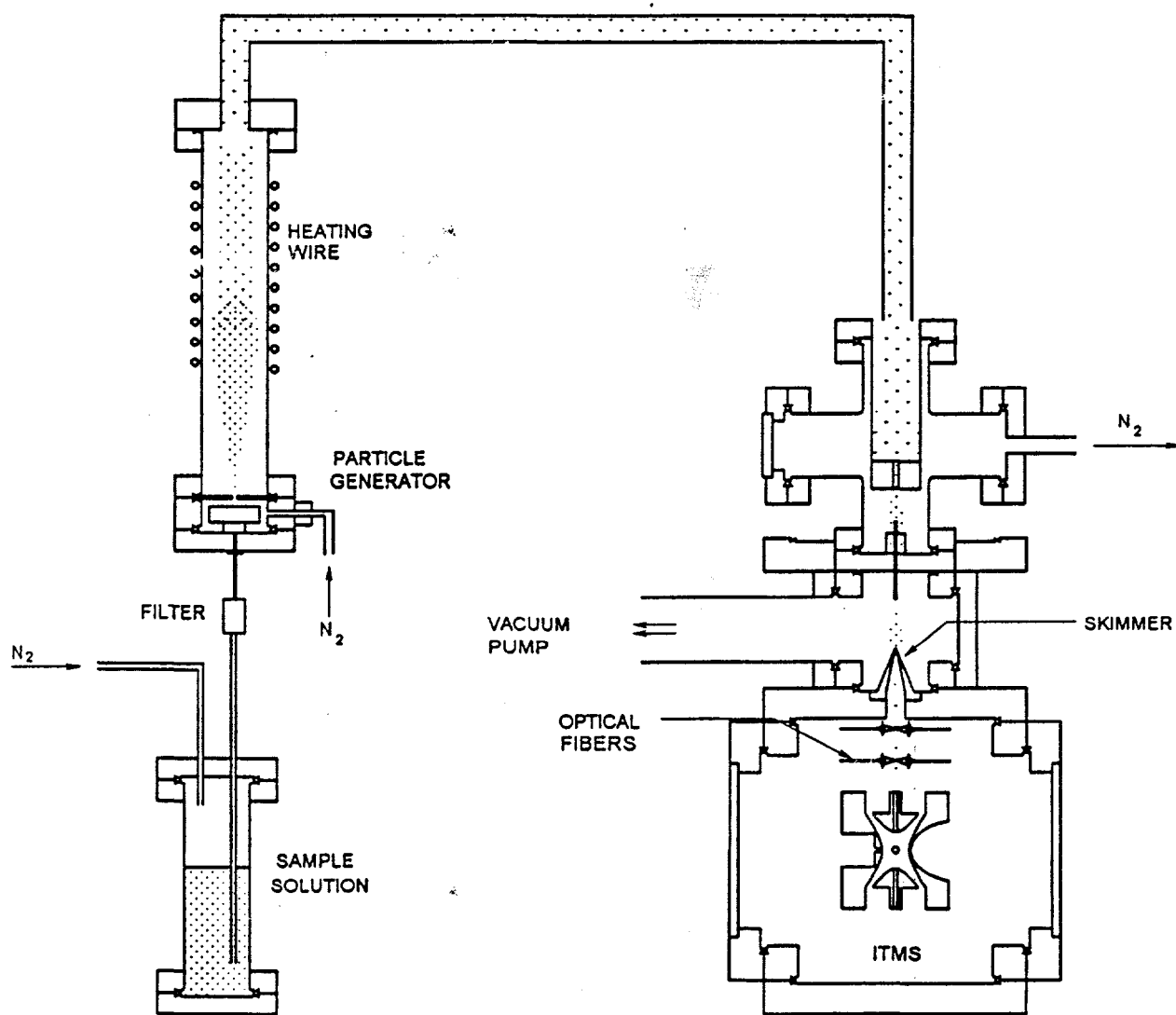


Figure 2. Experimental setup for real-time chemical analysis of aerosol particles.

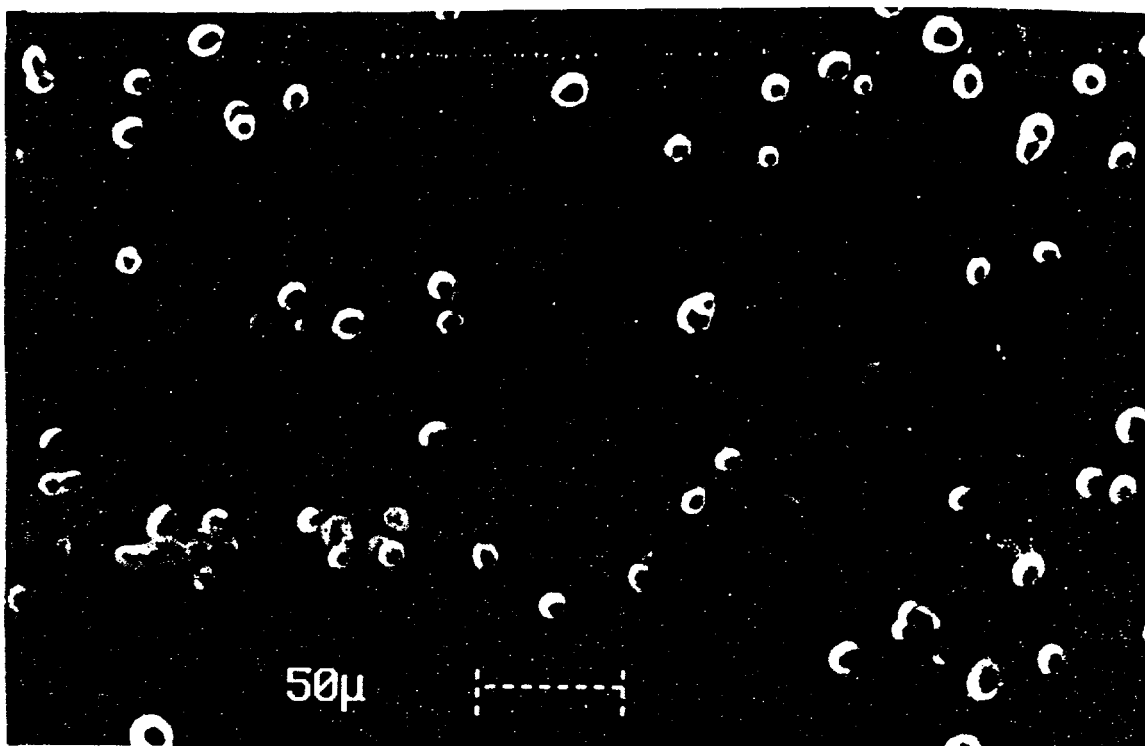


Figure 3. SEM picture of potassium nitrate salt particles produced by the particle generator.

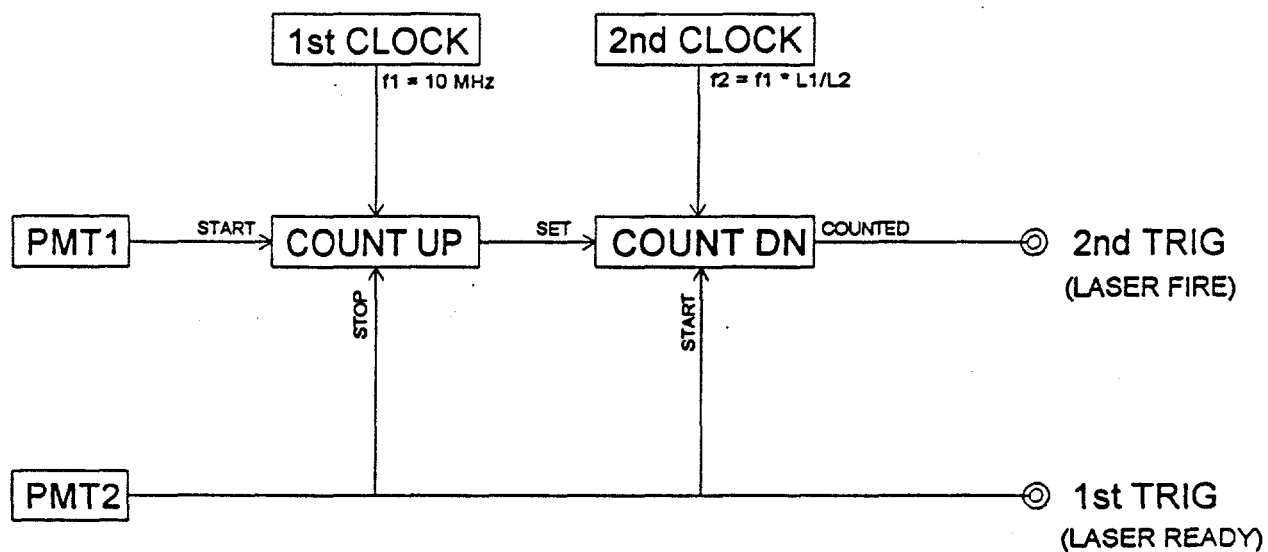


Figure 4. Schematic diagram of timing electronics.



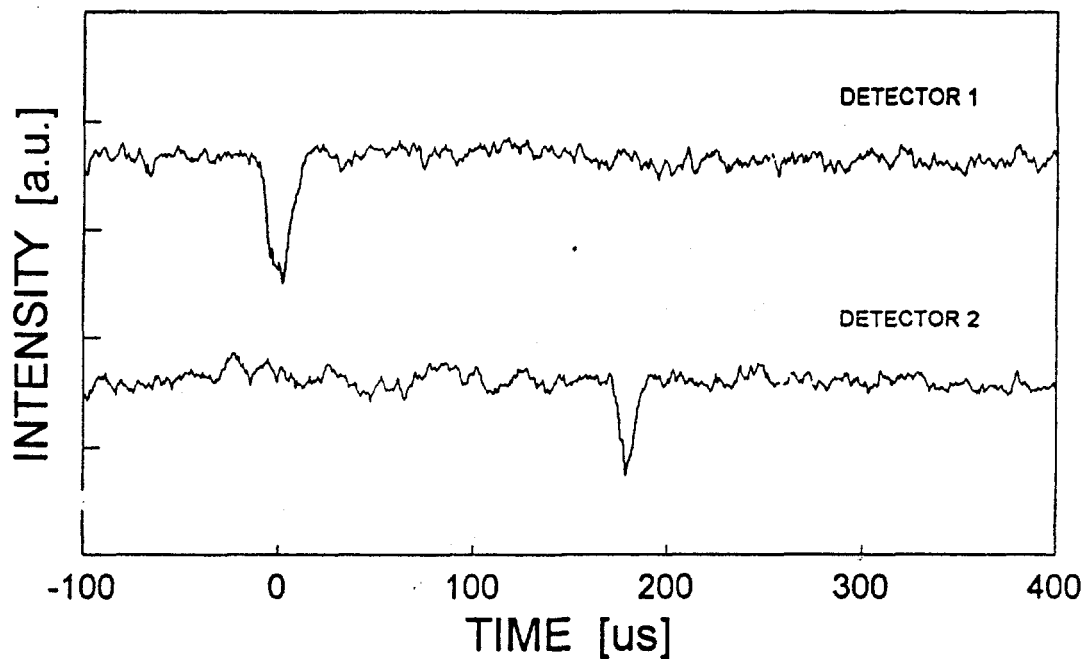


Figure 5. Coincidentally detected particle signals from the first detector (upper) and from the second detector (lower).

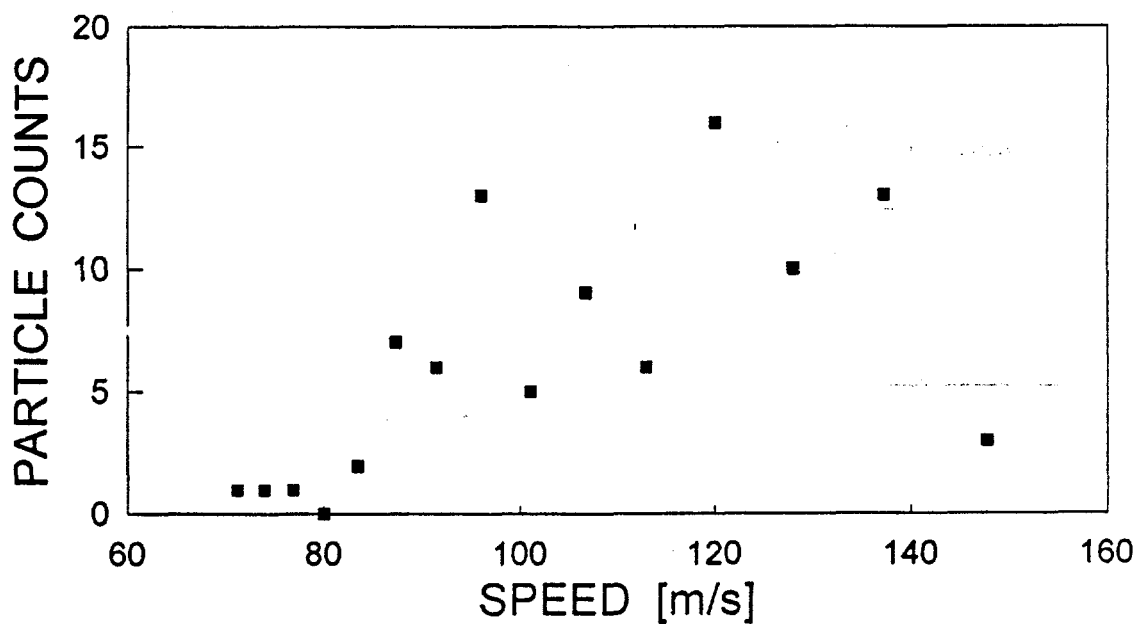


Figure 6. Speed distribution of potassium nitrate particles (15  $\mu\text{m}$ ) injected from the air to the vacuum chamber.

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