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Fite et al.

[11] **3,808,433**

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[54] **METHODS AND APPARATUS FOR DETECTION OF VERY SMALL PARTICULATE MATTER AND MACROMOLECULES**

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[52] **U.S. Cl.** **250/251,** 250/425

[51] **Int. Cl.** **G01m 27/78**

[58] **Field of Search** 250/251, 425; 73/28

[56] **References Cited**

UNITED STATES PATENTS

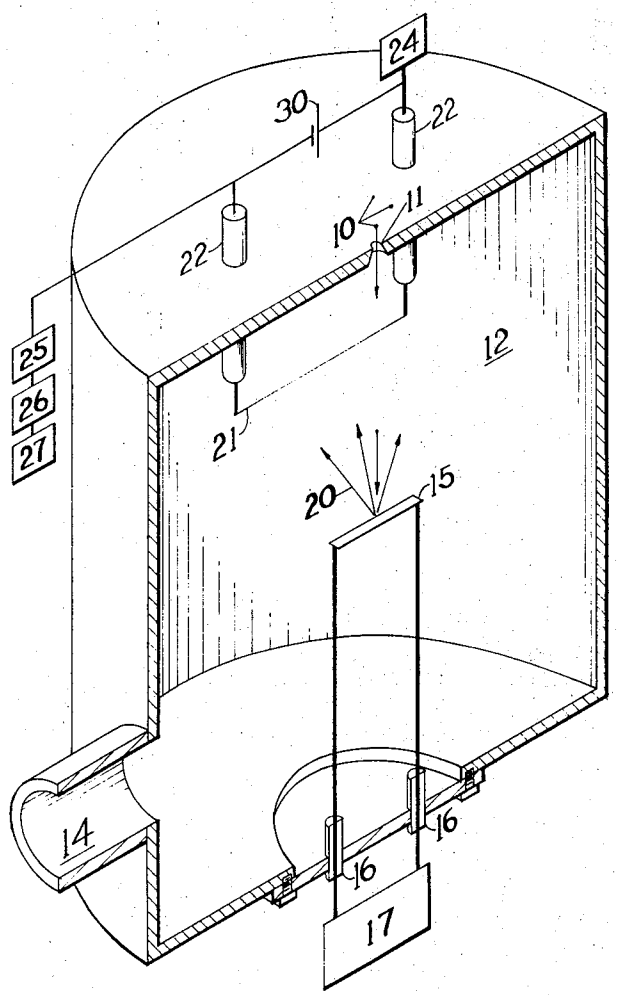
3,433,944	3/1969	George	250/251
3,336,475	8/1967	Kilpatrick	250/425
3,484,603	12/1969	Bloom et al.	250/251
3,300,640	1/1967	Eubank	250/251

Primary Examiner—Archie R. Borchelt
Assistant Examiner—B. C. Anderson
Attorney, Agent, or Firm—Mason, Mason & Albright

[57] **ABSTRACT**

A method and apparatus for detecting, sizing, and counting gas borne particulate matter are described. The particles are impacted onto a heated surface capable of pyrolyzing them. Some of the products of the pyrolysis are then surfaceionized, producing a burst of ions which is detected electronically producing a voltage pulse proportional to the amount of surface-ionizable matter originally present in the particle. Methods are described for adding to each particle an amount of surface-ionizable material proportional to the particle size, enabling the instrument to measure the particle size distribution of a collection of gas-borne particles. The basic apparatus may detect particles by means of either positive or negative surface-ionization, and is capable of operation either when situated in air or when located in a vacuum system.

51 Claims, 11 Drawing Figures



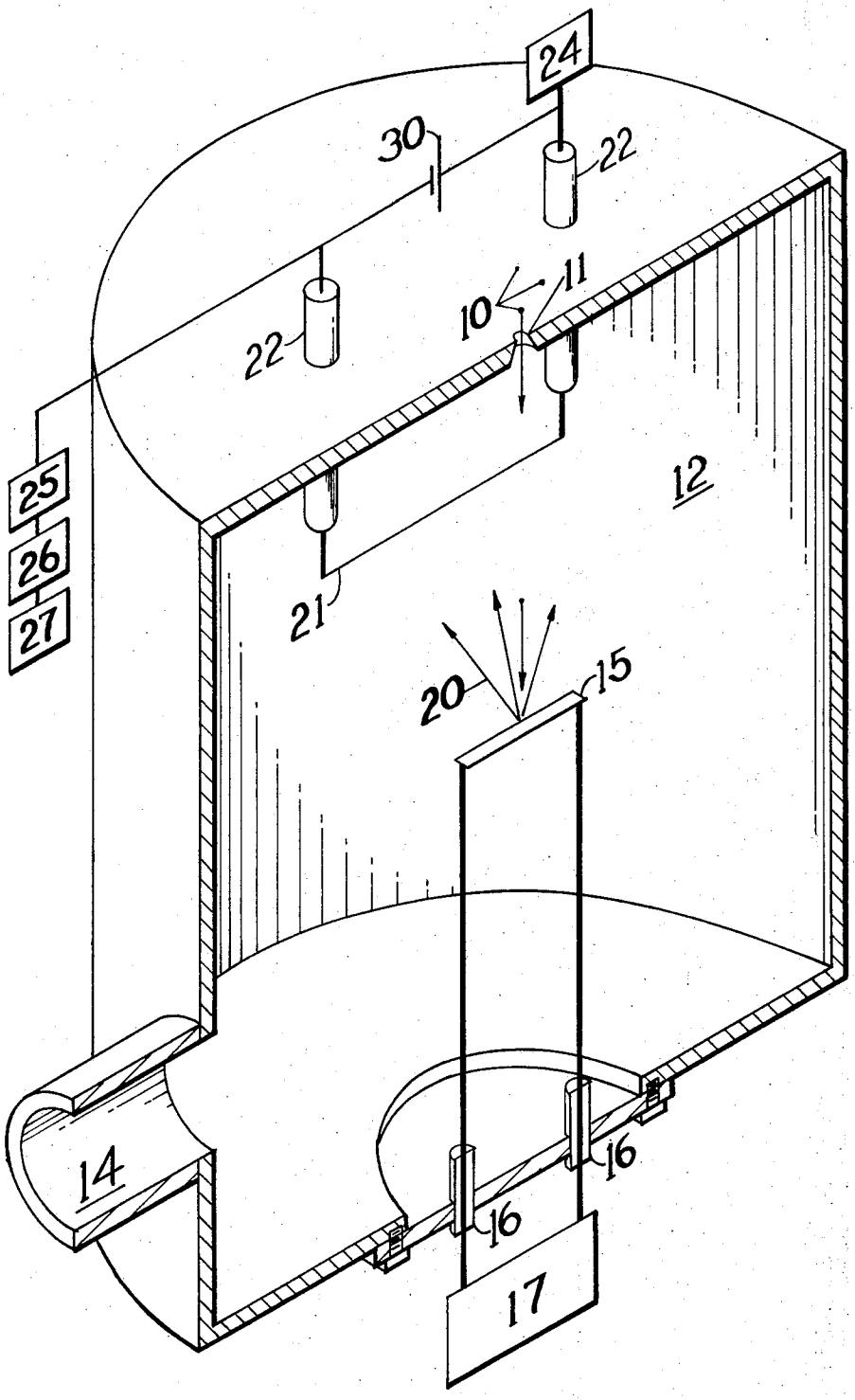


Fig. 1

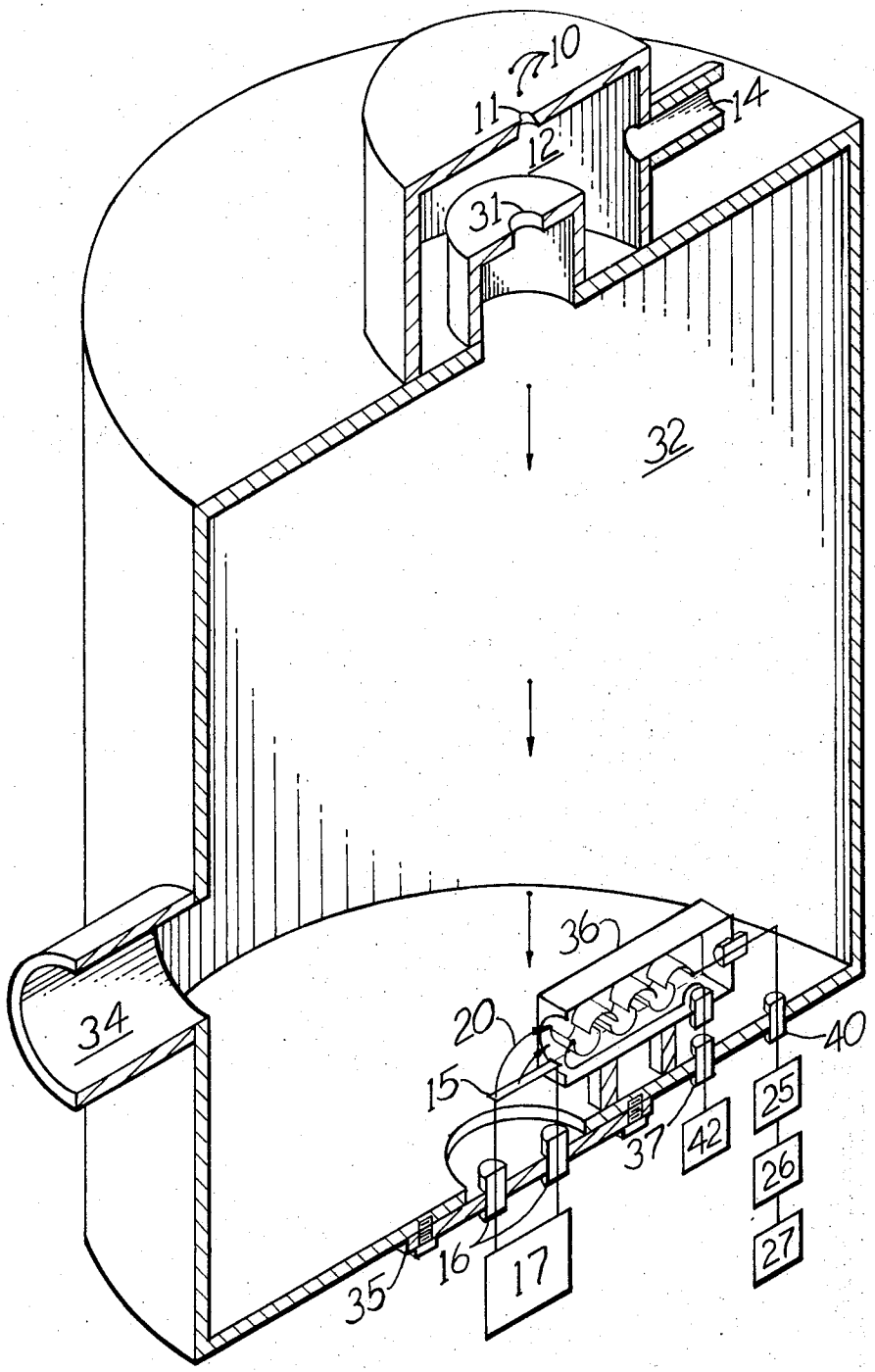


Fig. 2

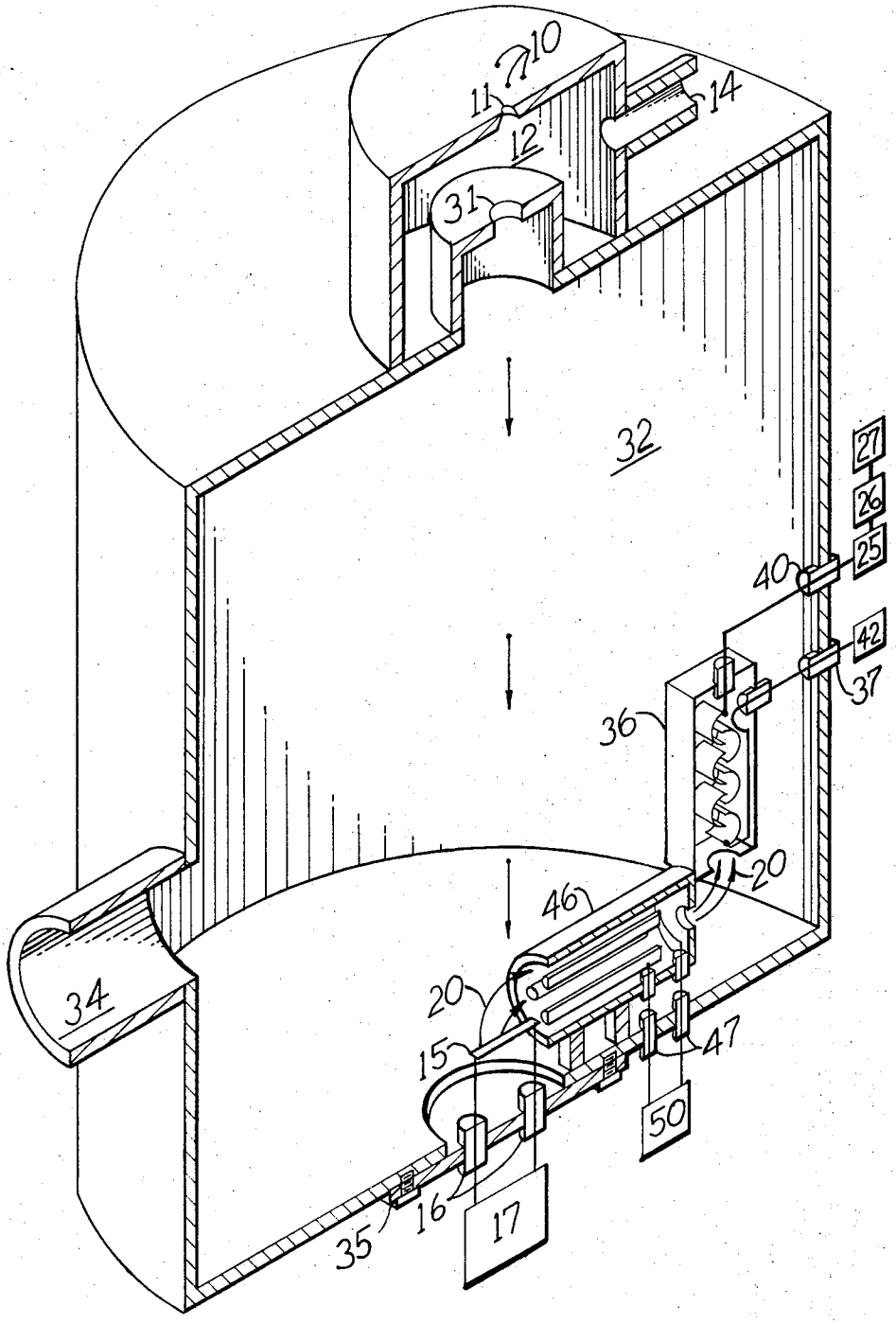


Fig. 3

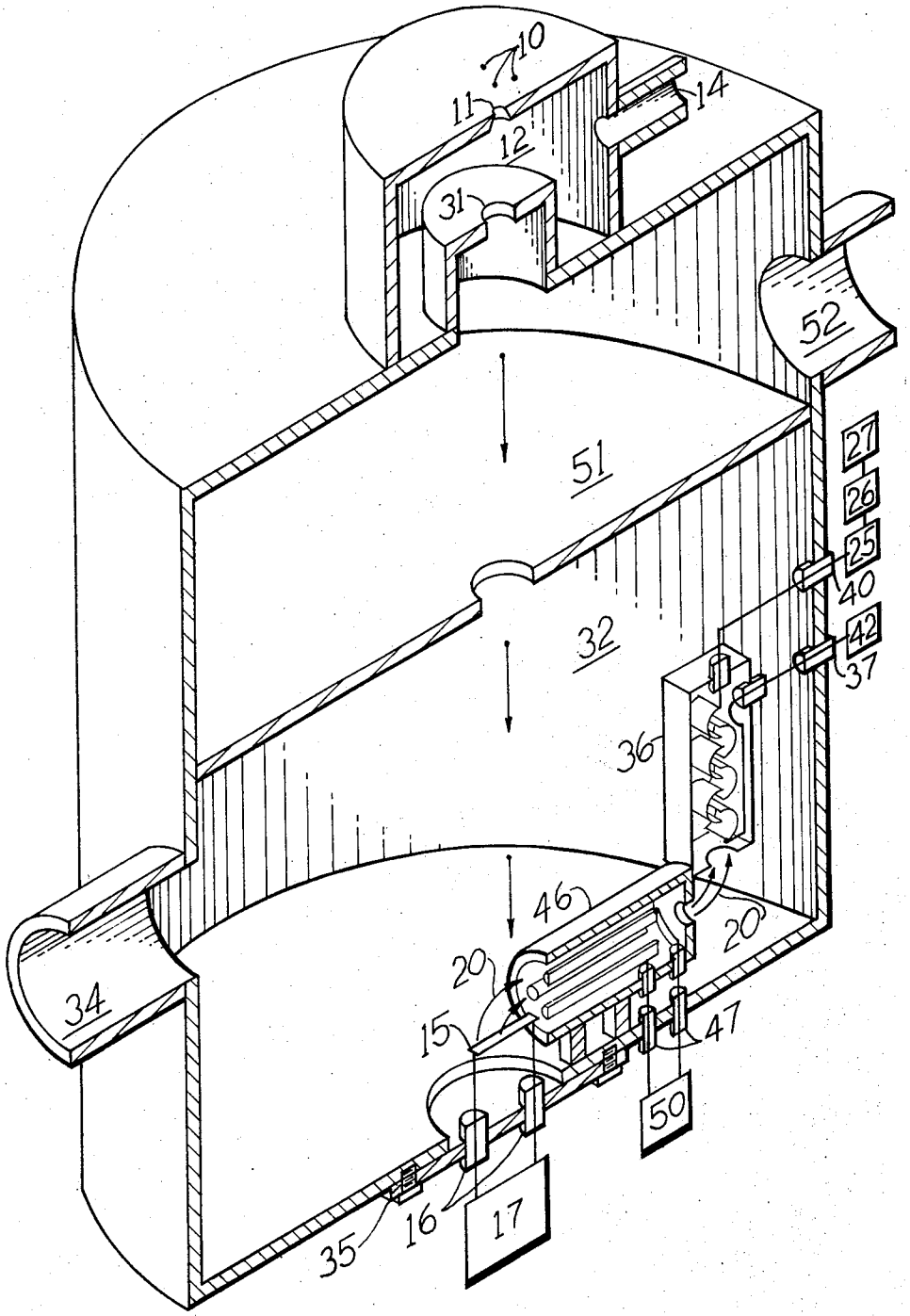

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Fig. 4

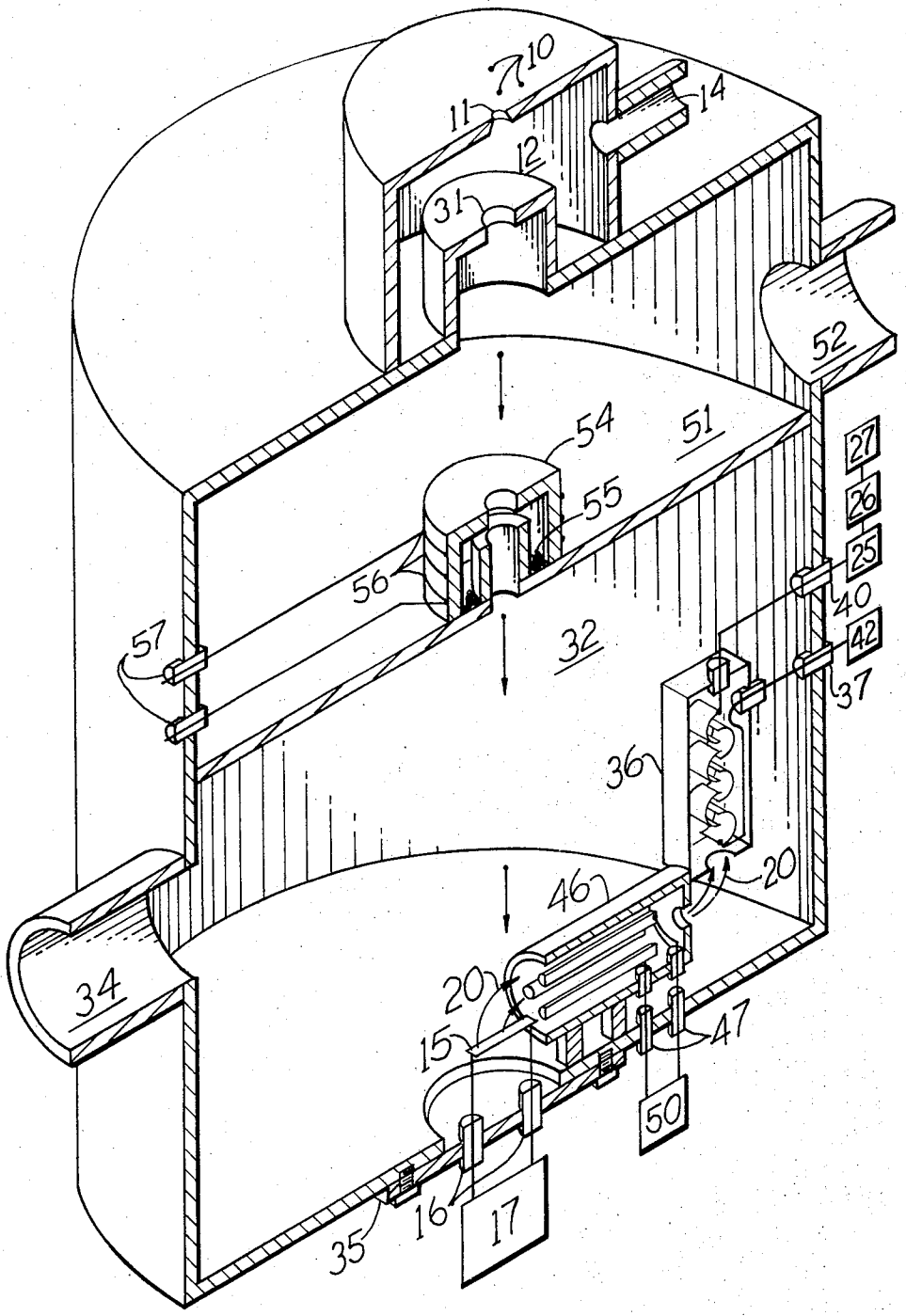

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Fig. 5

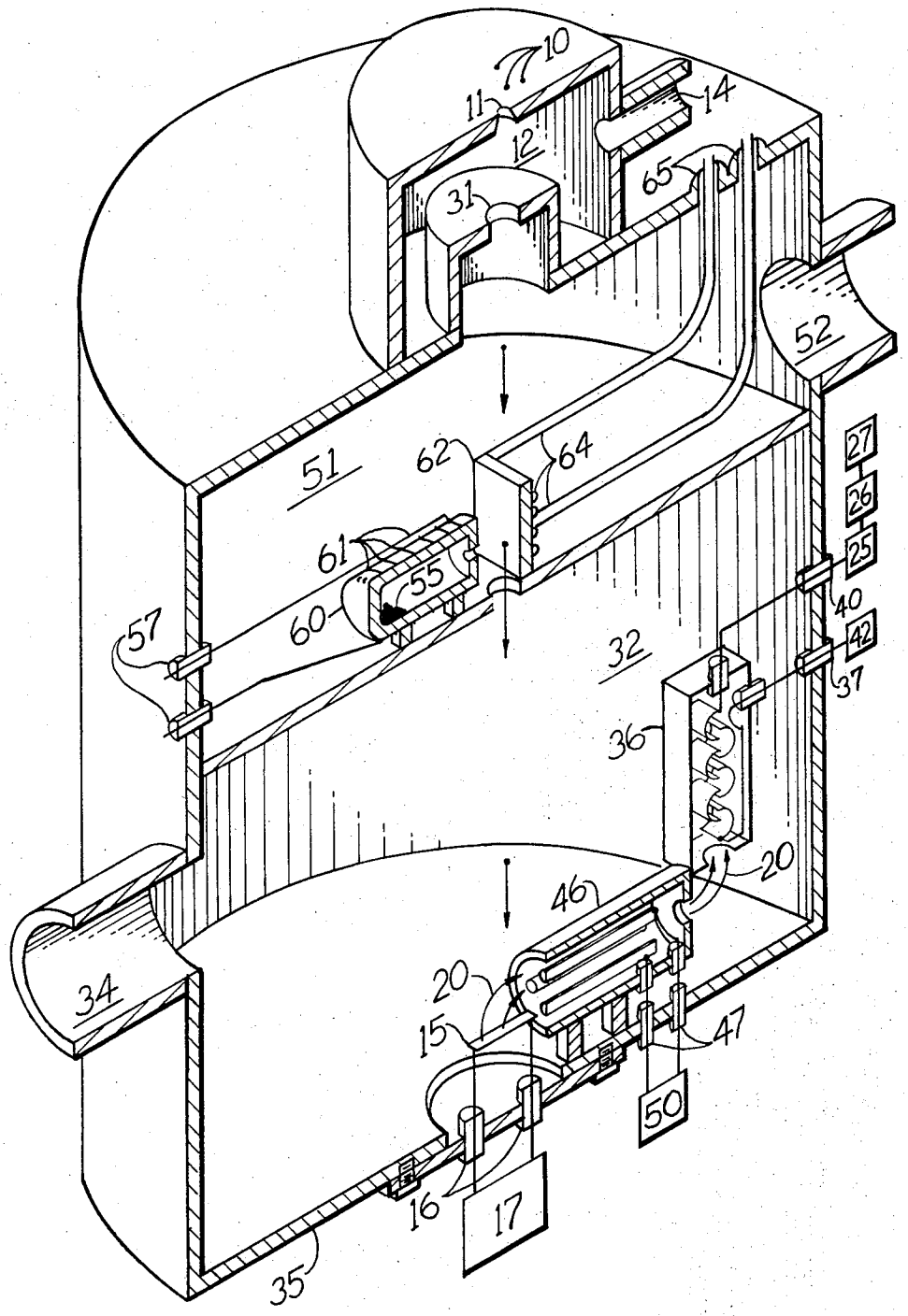

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Fig. 6

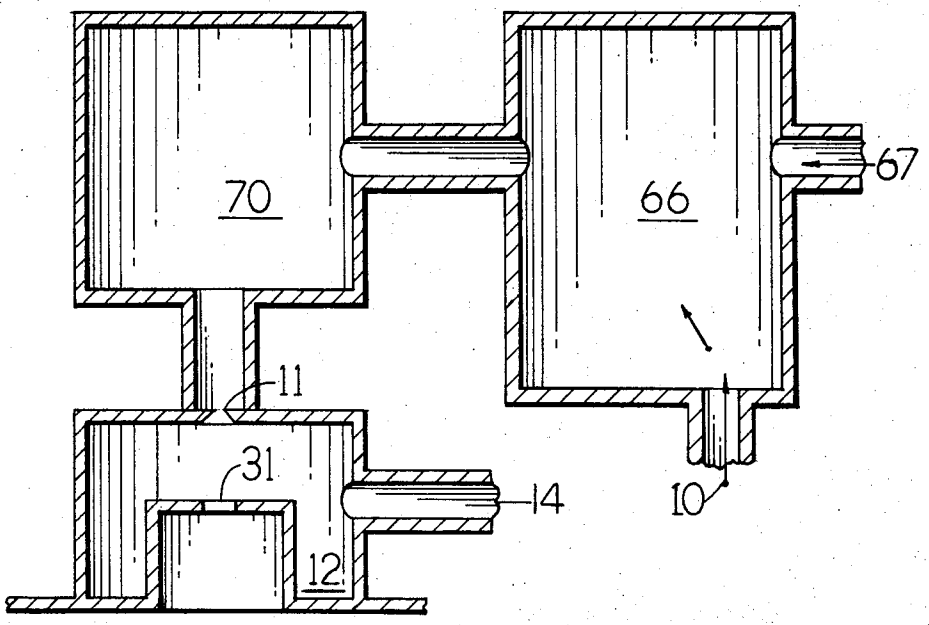


Fig. 7

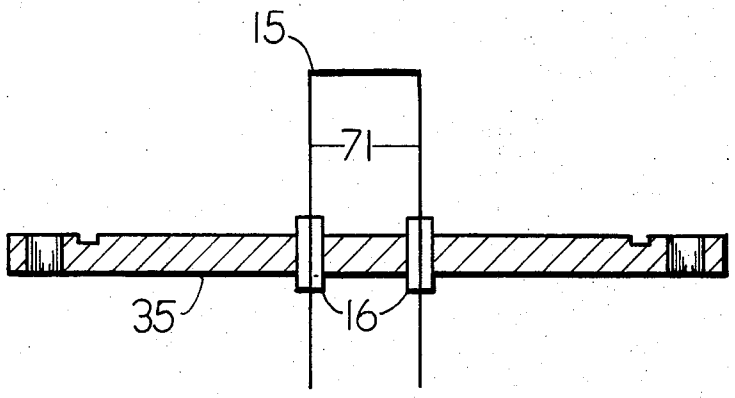


Fig. 8

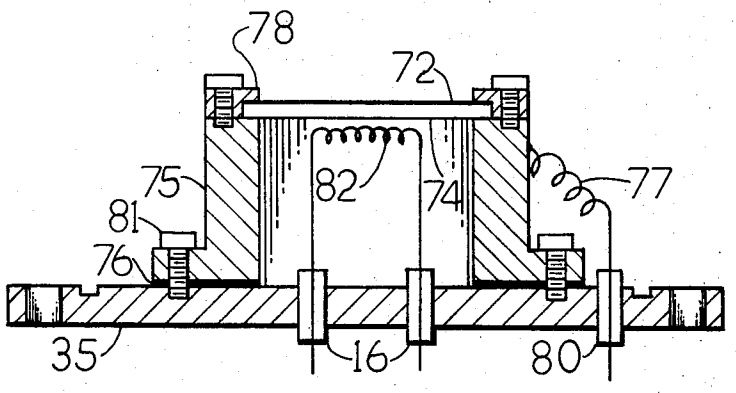


Fig. 9

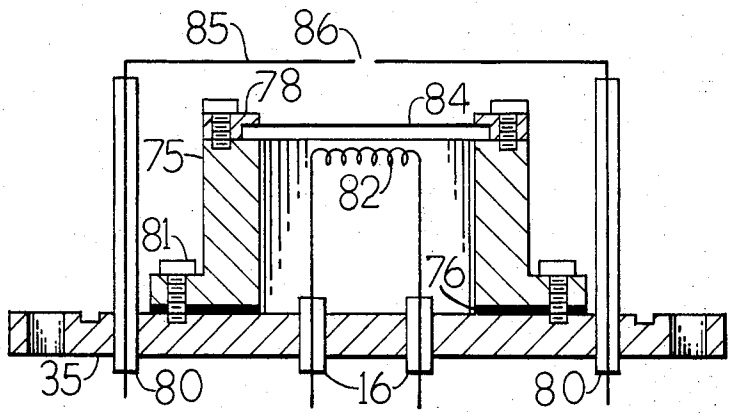


Fig 10

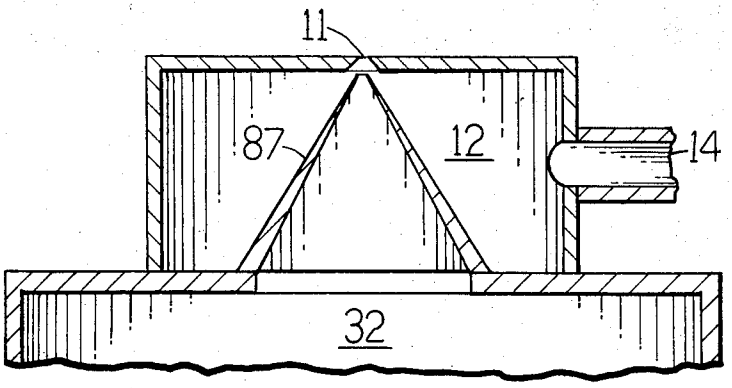


Fig. 11

METHODS AND APPARATUS FOR DETECTION OF VERY SMALL PARTICULATE MATTER AND MACROMOLECULES

BACKGROUND OF THE INVENTION

The detection and size determination of airborne particulate matter has been the object of considerable research in recent years. In U.S. Pat. No. 2,702,471, a device is described which can detect either (1) particles with low vaporization temperatures, such as water, or (2) particles which are readily combustible in air, such as oil, the size of either type of particle being of the order of tens of microns. U.S. Pat. Nos. 3,665,441, 3,178,930, and 3,679,973 describe devices which charge particles in an ionic discharge and then separate them according to ion mobility, and a device described in U.S. Pat. No. 3,628,139 utilizes the effect whereby an aerosol particle causes an avalanche breakdown in the carrier fluid. An apparatus described in U.S. Pat. No. 3,434,335 can acoustically detect particles with sizes of the order of tens of microns. The process whereby an aerosol particle can change the resonance frequency of a piezoelectric crystal is described in U.S. Pat. Nos. 3,561,253 and 3,653,253.

None of the devices described above has been demonstrated to detect efficiently particles smaller than a few tenths of a micron. Other conventional techniques such as light scattering and impingers also become less effective for smaller particles. Yet, these smaller particles may present a health hazard by penetrating to the deeper portions of the lungs and constitute an explosion hazard in mines by possessing a large surface-to-volume ratio. Particles smaller than a tenth of a micron are difficult to trap in filters or to remove from a gas by electrostatic precipitation. An effective method is thus needed for continuously detecting and counting very small particles. We have discovered that this can be accomplished in a novel and new manner by a process of pyrolysis on a hot surface, followed by surface ionization of some of the atoms of each particle. Such a method is described below and some typical apparatus are presented.

SUMMARY OF THE INVENTION

The invention relates to a new method and apparatus for detecting individual gasborne particles and/or macromolecules. The method essentially comprises bringing each particle into contact with heated surface capable of decomposing or vaporizing the particle and then surface-ionizing some of the atoms constituting the particle. The pulse of ions thus generated is detected by electronic means and converted into a signal which is stored in a scalar or other recording device with a requirement being that the pulse of ions generated by the particle be greater than the background pulses generated by the ions which are formed from impurities normally on and in the heated surface. A refinement of this method comprises use of a vacuum pump to partially evacuate the region in which the heated surface is located, with the gas containing and surrounding the particles being leaked into the partially evacuated region via a small aperture. This has the effect of reducing the viscous drag of the gas on the particles, enabling them to impact more efficiently onto the heated surface. Another refinement comprises use of a device such as an electron multiplier which has the effect of multiplying

the electric charge associated with each burst of ions by a factor of up to 10^6, hence creating a signal sufficiently large to be detected by electronic means. A further refinement comprises use of a mass analyzer to select one particular species, or a group of species of ions leaving the heated surface and reject all other ions, thus increasing the signal to noise ratio and hence the sensitivity of the instrument. A still further refinement consists of adding to each particle, prior to detection, an amount of some specific surface-ionizable substance, said amount being characteristic of the size of the particle. Upon impaction onto the heated surface, the size of the ion pulse generated will be characteristic of the size of the particle.

When an atom, such as sodium, having an ionization potential comparable with the work function (the energy with which the metal surface will hold an electron) of a metal, such as tungsten, comes into contact with that metal which is in a heated condition, the valance electron leaves the atom and enters the metal, with a positive sodium ion being reemitted into the gas phase. The resulting sodium ion is then detected through its electrical charge or upon being accelerated into an electron multiplier. The metal surface is heated to 800°–1,500° C. to establish rapid equilibration, and hence rapid response times. (For alkalis on tungsten at 1,400° C., the average time required for ionization and reemission after an atom strikes the surface is of the order of $10^{-4} - 10^{-5}$ sec.) Such surface ionization detectors have long been in use to detect beams of alkali atoms and their compounds. In addition, many of the alkali halides, certain other atoms of low ionization potentials, and some hydrocarbon molecules and radicals can be detected in this manner.

A similar phenomenon operates to produce negative ions when an atom such as chlorine impinges upon a heated surface having a work function comparable to the electron affinity of the incident atom. In this case, an electron leaves the hot metal and attaches to the chlorine atom, forming a negative chlorine ion which can be detected by its negative charge. The halides, some alkali halides, and certain other molecules containing electronegative radicals such as CN with high electron affinities have been detected in this manner.

In both positive and negative surface ionization, the the temperature of the metal is ordinarily below that at which appreciable thermionic electron emission occurs. In addition, any electrons that are emitted are removed or trapped by applying an appropriate magnetic field that affects the light electrons, but not the heavier ions.

The selection of the metal is dictated by its work function, which should be large for positive ion detection and small for negative ion detection, and by the environment in which it is to operate. For particles which are to be detected in vacuum through positive ion detection, tungsten is a satisfactory material whereas the high resistance to oxidation of iridium, rhenium, rhodium, and platinum makes these materials preferable for operation in air. For negative ion detection, surfaces such as thoriated tungsten are suitable for operation in vacuum, whereas for negative ion detection in air, materials such as barium zirconate may be used.

In the normal metals such as tungsten, there are always impurities, some of which are alkali and halogen atoms. Upon heating the metal, these diffuse to the sur-

face where they surface-ionize and emit a constant current of positive or negative ions. A particularly troublesome species in the case of tungsten is potassium, which is emitted in bursts of up to 10^6 ions, with the duration of the bursts ≈ 50 microseconds (μs). This background emission can be reduced by "conditioning" the metal, i.e., by keeping it hot for many hours. An alternative method is to deposit pure metal on the surface through the pyrolytic decomposition of a compound such as tungsten hexacarbonyl, which can be administered to the surface either continuously or in cycles. This second technique has been found to suppress the bursts of potassium ions (K^+), resulting in both a reduced background signal and a Poisson (random) distribution for the emission of the K^+ ions.

A series of events is said to be random if the probability of an event occurring during a given time depends only on the length of that period of time, and is completely independent of whether any other similar events occur during the same period. Under these circumstances, the probability P_n that n events will occur during a time interval τ is given by the Poisson distribution function $P_n = e^{-\bar{n}} n/n'.$, where $\bar{n}$ is the average number of events for the time interval τ.

If a particle or macromolecule containing some atoms (molecules) of a surface-ionizable element (compound) arrives at a suitable hot surface, these atoms (molecules) can be surface ionized within a short period of time. A typical particle heats up to within 90 percent of the surface temperature within several microseconds, and individual alkali atoms tend to be surfaceionized within a time of 10 to 100 μs. This clustering in time of ions which originate from a particle or macromolecule provides a powerful technique for distinguishing between the ions which come from the heated metal surface itself and those which originate from a particle.

Suppose the ion detector apparatus is made to perform electrical integration over, say 10 microseconds. If the background signal from the metal surface has been reduced through conditioning or deposition of a fresh surface to 5×10^6 ions/sec, then the average number of background counts during one time constant of the detector will be $(5 \times 10^6)(10^{-5}) = 50$ counts/10μs. This causes the detector to put out an average signal corresponding to 50 counts, with fluctuations corresponding to a random distribution of arrival of background ions. For example, if the average number of counts per 10 microseconds is 50 ions, then the probability of getting 100 or more counts during 10 microseconds is

$$\sum_{n=100}^{\infty} e^{-50} \frac{50^n}{n!} \simeq 4 \times 10^{-8},$$

or about 1 such count per 200 seconds on the average. Owing to a slightly non-Poisson distribution of the background ions due to incomplete suppression of the alkali pulses mentioned earlier the average time period for such a count in actual practice is somewhat less. Nevertheless, the arrivel at the filament of a particle capable of emitting 50 or more ions during the 10 μs produces an effect which is only rarely exhibited by the background ions. By sending the output signal from the ion detector through a pulse height discriminator set to reject the background pulses, the arrival of a large particle can be noted and registered on a recording device.

As an example of the detection of heavy particles in air, suppose we are dealing with particles of 0.1 micron radius which contain 10 parts per million of, say, sodium (Na; atomic mass 23). Assuming a particle density of 5 gram/cm^3, the number of sodium atoms available for surface-ionization is 4/3 $(10^{-5}$ cm$)^3$ (5 gm/cm^3) (10^{-5}) (1 amu/1.67 $\times$ 10^{-24} gm) (1 atom/23 amu) $\simeq$ 5 $\times$ 10^3 sodium atoms. When these atoms are surface-ionized and then collected at an electrode with a capacitance of 0.5×10^{-12} farad, the voltage pulse developed across the capacitor will be $\Delta V = \Delta Q/C = (5 \times 10^3$ ions) $(1.6 \times 10^{-19}$ coulombs/ion) $(0.5 \times 10^{-12}$ farad$)^{-1} \simeq 1.5 \times 10^{-4}$ volts, a signal which is detectable by electronic means. Since at atmospheric pressure ions tend to diffuse rather slowly (the ionic mobility M_O for sodium ions in nitrogen gas at room temperature and pressure in an electric field E is about $M_O = 3.0$ cm^2 volt^{-1} sec^{-1} E) it is usually necessary to apply a suitable voltage to either the heated surface or the collecting electrode or both, so as to produce an electric field which causes the ions to reach the collector in a reasonable period of time. For example, if the heated surface and the collector are 0.5 cm apart and the applied voltage difference is 2,000 volts, then the time t required for the ions to reach the collector will be $t = d/(M_O E = (0.5$ cm) (3.0 cm^{2}volt^{-1} sec^{-1})$^{-1}$(2 $\times$ 10^3 volts/0.5 cm)$^{-1} = 40$ μs. This enables the burst of ions released from the heavy particle to be distinguished from the background noise by means of the pulse-counting method discussed earlier.

When the number of ions released by a particle is too small to produce a measurable voltage pulse at the collecting electrode, the particle can still be detected by utilizing some method of causing the original burst of ions to become increased in number during the transit from the heated surface to the collector. One such method comprises increasing the electric field to a value slightly below that at which the air breaks down but at a value at which the introduction of the charge from a burst of ions causes an avalanche breakdown of the carrier gas, producing many more ions. By methods well known in the art, the electric field is momentarily reduced by means of an external quenching circuit just after each breakdown begins, quenching the breakdown and preparing the detector for the next particle.

A major difficulty in detecting gasborne particles is that, as the particle size decreases, the inertia of each particle decreases as the cube of the particle radius, while the viscous forces exerted by the carrier gas decrease only as the first power of the particle radius. As a result, sufficiently small particles suspended in a moving gas will not readily deposit on any surfaces, but will instead tend to follow the streamlines of the carrier gas. According to Fuks, Mechanics of Aerosols, Pergamon, p. 173, in order for particles of radius r and density γ, moving in an airstream of speed V_O, viscosity n and at atmospheric pressure to impact with efficiency greater than 50 percent onto a long perpendicularly oriented flat ribbon of width w, the airstream velocity V_O must be in excess of $V_O = 9\eta w/(r^2\gamma)$. For a 1 micron ($\mu$) particle with $\gamma = 1$ gm/cm^3 moving in air with visocity $\eta =$ 185 micropoise, the velocity of the airstream required for 50 percent deposition on a 2 mm ribbon is about 3 $\times$ 10^4 cm/sec, a difficult speed to obtain at atmospheric pressure. For a particle ten times smaller, the speed required increases by a factor of 100. One solution to this

problem comprises placing the heated surface into a chamber in which is maintained a partial vacuum and leaking the carrier gas with its suspended particles into the vacuum chamber through a small aperture in fluid communication with the sample. If, for instance, the pressure in the vacuum chamber is reduced to one torr (1 mm of mercury), then it can be shown that a 1 micron particle of density 1 gm/cm^3 traveling 5 cm through the chamber can have its velocity reduced by at most 8 percent prior to striking the heated surface. For smaller particles, the vacuum can in principle always be improved sufficiently to ensure impaction onto the heated surface.

The method by which required pumping seeds are calculated will be briefly discussed. If gas from an initial pressure P_o leaks with a speed S_o liters/sec into a chamber which is at a lower pressure P_1 due to being pumped at a speed S_1 liters/sec by a vacuum pump, then in the steady state, conservation of mass flow necessitates the relationship $P_oS_o = P_1S_1$. As an example, if 10 cm^3/sec of air at atmospheric pressure are being leaked into a chamber which is being evacuated by means of a mechanical vacuum pump with a pumping speed of 25 liters/sec, then the steady-state pressure in the chamber will be P = (1 atmosphere) $(10^{-2}$ liters/sec) (25 liters/sec)$^{-1} = 4 \times 10^{-4}$ atmosphere. A well rounded aperture will leak about 20 liters/sec of air per cm^2 of aperture area from atmospheric pressure into any pressure less than about 10 torr (mm of mercury). Thus the size of aperture required to leak the above 10 cm^3/sec into a chamber is A = $(10^{-21}$ liter/sec) (20 liter/sec-cm^2)$^{-1} = 5 \times 10^{-4}$ cm^2, corresponding to an aperture diameter of about 0.3 mm.

If a high vacuum is required, and if for this purpose two chambers having pressures of P_1 and P_2 of background gas are separated by an aperture of area a, with chamber 2 being evacuated by means of a diffusion pump with a pumping speed of S_2, then $\frac{1}{4}(p_1 - p_2)\bar{c}a = P_2S_2$, where $\bar{c}$ is the average molecular speed of the background gas. For instance, if $P_1 = 10^{-3}$ torr, $\bar{c} = 10^5$ cm/sec, $S_2 = 10^5$ cm^3/sec, and we wish to have P_2 less than 5×10^{-5} torr, then the maximum aperture diameter allowable is: $a = (5 \times 10^{-5}$ torr) $(10^5$ cm^3/sec (4) $(95 \times 10^{-5}$ torr)$^{-1}$ $(10^5$ cm/sec)$^{-1} = 0.21$ cm^2.

If the vacuum in the region of the heated surface is improved to less than 10^{-4} mm of mercury, the ions emitted from the surface can be accelerated into an electron multiplier, which is adapted, to deliver an output charge of the order of 10^6 times the charge contained in the burst of ions. A pulse height discriminator followed by a scalar or other recording device takes the output signal from the electron multiplier and registers the arrival of the particle.

It usually happens that the metal surface produces ions which comprise predominantly several species, e.g., for most tungsten surfaces, sodium ions, Na^+, and potassium ions, K^+, constitute about 90 percent of the background. Hence, an improvement in the sensitivity and the signal-to-noise ratio is accomplished by taking the ions produced by surface ionization through an ion mass analyzer (mass spectrometer) prior to their reaching the electron multiplier. As an illustration, with a hot tungsten surface which produces 5×10^6 counts/sec of total background (sodium, potassium, and other metallic and organic ions) but only 5×10^4 counts/sec of cesium ions (Cs^+). When a particle containing Cs impurities arrives then, without mass analysis the particle must release 50 Cs^+ ions/10μS or more to be counted above the total background. By interposing an ion mass analysis device which is tuned to pass only cesium ions (thereby preventing the larger currents due to other ionic species from reaching the multiplier), the number of cesium ions which need be released for detection over the background signal fluctuations is much smaller. Since $\bar{n}$ (background Cs^+) in this case is 0.5 pulses/10μs, the probability for 10 or more background counts during 10μs is equal to

$$P_{n \geq 10} = \sum_{n=10}^{\infty} \frac{1}{e} \frac{1}{2n!} \simeq 10^{-9}$$

or one such count every 10^4 seconds. Hence one heavy particle need release only 10 (or fewer, if a smaller signal/noise ratio is permitted) Cs^+ ions in order to be counted above the background.

Most inorganic particulate matter (e.g., dust or smoke particles) contains naturally occurring impurities such as alkali metals, halogens, and hydrocarbons in sufficient quantity that the particles are immediately detectable without any further treatment of the particles. Organic materials such as macromolecules frequently contain halogens or cyanogen radicals (CN) in sufficient quantities to produce detectable signals of CN^- or halogen nagative ions or more complicated negative ions. It has also been found that many organic molecules can be surfaceionized so that a long macromolecule stands a good chance of breaking into fragments, with some of the fragments being ions.

If a particle does not contain sufficient naturally occurring surface-ionizable impurities for the detection sensitivity available, the signal can be increased by "tagging." This procedure consists of passing the particle through either a chamber containing a vapor of surface-ionizable atoms (molecules), or through a crossed atomic (molecular) beam of a surface ionizable element (compound). Atoms (molecules) from the vapor or atomic (molecular) beam strike the particle and are adsorbed onto the surface. The tagged particle, its surface enriched with surface-ionizable atoms (molecules), then moves to the hot metal surface where it releases its tagging atoms (molecules) as a burst of ions.

Through such tagging techniques it is possible to measure the geometrical cross section, and therefore the size of a particle, inasmuch as the size of the ion burst depends on the number of surface-ionizable atoms delivered to the hot surface by the particle, and that number is directly proportional to the surface area of the particle while in the tagging chamber. A final advantage is that one can choose for the tagging species a substance not present in the normal background from the heated metal detector surface, and thus obtain an improved signal-to-noise ratio.

Macromolecules and large biological molecules are also detectable by the tagging approach. One technique is chemically to substitute the tagging species for an atom in the molecule being tagged, e.g., substitute a fluorine atom for a hydrogen atom in a methyl group. Another method is to attach the tagging atom or molecule to the macromolecule by a chemical bond, e.g., it has been found that a cesium atom will attach itself to an aromatic or heterocyclic ring (e.g., a nucleic acid molecule) via a weak resonance bond.

In view of the foregoing, it is a principal object of this invention to provide a new method and apparatus for electrically detecting a very small particulate matter and macromolecules suspended in a gaseous medium. A further object is to detect said particles by means of their naturally occurring surface-ionizable constitutents. A still further object of the invention is to add to such particles additional surface-ionizable materials which can supplement the naturally occurring ones. A yet further object is to use the amount of additional material added to each particle as a measure of the size of said particle.

Other objects and advantages of the invention will become known by reference to the following description of some typical apparatus and the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an isometric representation in partial section of one form of the invention in which the particles are drawn into a chamber, which may be either at atmospheric pressure or at a partial vacuum, and impinged onto a heated surface where they produce bursts of ions which are collected onto an electrode.

FIG. 2 is an isometric representation in partial section of a form of the invention in which the particles are introduced into a vacuum system and impinged onto a heated surface where they produce bursts of ions which are detected by a particle multiplier;

FIG. 3 is an isometric representation similar to that in FIG. 2 except that there is interposed a mass analyzing device which transmits one particular species, or several particular species, of those ions which leave the heated surface;

FIG. 4 represents a form of the invention similar to that represented by FIG. 3 excpet that there is added an intermediate chamber and vacuum pump to provide a better vacuum in the detection region and/or to permit a larger initial aperture into the vacuum system;

FIG. 5 illustrates a further form of the invention similar to that in FIG. 4 which illustrates the addition of a tagging chamber which adds to the surface of each particle, subsequent to the injection of said particle into the vacuum chamber, a specific surface-ionizable substance;

FIG. 6 is a cross-sectional isometric view illustrating another method by which the particles can be tagged within the vacuum system;

FIG. 7 is a cross-sectional partial view showing the top of FIG. 4 with additional structure of a means of tagging each particle prior to entry into the vacuum system included;

FIG. 8 is a cross-sectional view of the heated surface shown in FIG. 1;

FIG. 9 is a sectional view representing another embodiment of the heated surface;

FIG. 10 is a sectional view representing a further embodiment of the heated surface; and

FIG. 11 is a sectional view illustrating another construction of the upper portion of FIG. 2.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In FIG. 1 there is illustrated one embodiment of the invention in which particles **10** suspended in a carrier gas are drawn through an aperture **11** into a chamber **12** which is continuously being flushed by an exit tube **14** which is connected to a suitable exhaust fan. While in the chamber **12**, some of the particles **10** impact onto a heated surface **15**, which is mounted onto two feedthroughs **16**, allowing electrical connections to be made to a power supply **17**, capable of providing the current needed to heat the surface. Upon impinging onto the surface **15**, each particle releases a burst of ions **20** which is collected onto an off-axis electrode **21** mounted onto two feedthroughs **22** and to which a voltage is applied so as to attract the burst of ions, said voltage being applied through one of the feedthroughs **22** from a high-impedance voltage supply **24**. The arrival of each burst of ions **20** onto the electrode **21** produces a voltage pulse which is detected by a sensitive preamplifier **25**, the input resistance of which, coupled with the innate capacitance with respect to earth of the detector apparatus, determines the integrating time constant of the system. The integrated signal is then taken into a pulse height analyzer **26**, a circuit which can be one of a number of variations known to the skill of the art, the function of which is to sort signal pulses according to size and to exclude random background counts, thus providing a pulse height distribution curve which can be presented on on an appropriate display instrument **27**. The tendency of the collecting electrode **21** to become contaminated can be avoided by keeping said electrode sufficiently warm as to reevaporate any collected impurities. One means for accomplishing this comprises passing a current through the electrode **21** by means of a battery **30** connected to the feedthroughs **22**.

In one of several specific embodiments which have been used in our laboratories, the particles **10** have been coal dust, iron carbonyl powder, talcum powder, submicron polystyrene spheres, cigatette smoke, and aerosol crystals of sodium chloride (NaCl), cesium chloride (CsCl), sodium iodide (NaI), potassium chloride (KCl), sodium cyanide (NaCN), etc. The heated surface **15** was sometimes a directly heated iridium ribbon or wire and other times an indirectly heated film of platinum or tungsten oxide mounted on a substrate of quartz glass. The collecting electrode **21** was sometimes an irridium strip and sometimes a platinum wire. The distance between the heated surface **15** and the collecting electrode **21** was varied from 2 mm to 1 cm, with the voltage differences varying from 0 to $\pm$ 3,000 volts. The preamplifier **25** was of a standard commercially available type with integrating time variable from 10^{-6} to 10^{-3} sec. Some usable pulse-height analyzing devices **26** ranged from the triggering level on a scope to a multichannel analyzer. Display instruments **27** used scalers and chart recorders. It was found necessary to shield the system electrically to void pickup signals from line voltages, other instruments, etc.

When the voltage between the heated surface and the collecting electrode was increased to near 3,000 volts across a gap of about 1 mm, it was observed that small discharges occur whenever smoke is blown onto the heated surface. it is considered that, inasmuch as the amount of electric charge associated with each discharge is many orders of magnitude greater than the charge associated with each burst of ions from a single particle, the counting of such discharges provides a useful means of counting the particles which have the capacity to cause such discharges.

In a further set of experiments, the exit tube **14** was connected to a mechanical vacuum pump with a pump-

ing speed of 25 liters per second, and the entrance aperture 12 was made about 0.5 mm in diameter, leading to a steady-state pressure of about 5 torr. Under these conditions, the voltage difference between the heated surface and the collecting electrode needed to move the ions to the collecting electrode is considerably reduced. In addition, the voltage required to utilize the breakdown technique discussed above is much lower at these pressures.

Upon evacuating the region in which the heated surface is located to 10^{-4} torr, it still was found possible to detect pulses of ions on the collecting electrode when coal dust, cigarette smoke, iron powder, and aerosol crystals of the alkali halides were leaked into the vacuum system. The pulse heights were of the same size as those found in air (provided the electric fields in the latter case were kept below the breakdown threshold) but with a shorter rise time, corresponding to the greater mobility of ions in a vacuum.

In FIG. 2 there is illustrated one embodiment of the invention in which particles 10 suspended in a carrier gas are allowed to pass through a small aperture 11 into a partially evacuated chamber 12, being continuously evacuated through a tube 14 connected to the intake of a suitable vacuum pump. Most of the carrier gas is pumped away through the tube 14, while particles 10, by virtue of their greater inertia, travel in a straight line to an aperture 31 which separates chamber 12 from another chamber 32 maintained at a higher vacuum suitable for the operation of the apparatus. The second chamber 32 is evacuated through a duct 34 which leads to a suitable vacuum pump. Particles 10 then impinge upon the surface of a heated material 15 which is mounted on two feedthroughs 16 providing electrical connections through a flange 35. The heater power is provided from a suitable power supply 17. It will be understood that material 15 may be heated directly or indirectly. Particles 10, upon impinging upon heated surface 15, emit bursts of ions 20, which are driven by electric fields into a particle multiplier 36. Any one of a number of types of particle multipliers, the operation of which are well known in the art, may be utilized for this purpose. The voltage required to operate the multiplier is administered through a feedthrough 37 in the wall of vacuum chamber 32 from a suitable power supply 42. The output signal of particle multiplier 36 is taken to the outside of the system through a coaxial feedthrough 40, leading to a preamplifier 25, the input resistance of which, coupled with the innate capacitance of the signal cable, determines the integrating time constant of the detecting system. The integrated signal is then taken into a pulse height analyzer 26, the circuit for which can be one of a number of variations within the skill of the art and the function of which is to sort signal pulses according to size and thus exclude random counts and provide a particle size distribution curve which can be presented on an appropriate display instrument 27.

A specific embodiment of this design, one of several which have been successfully used in these laboratories, will be briefly discussed. Particles 10 have been coal dust, iron carbonyl powder (3–5 microns, diameter), talcum powder, powdered bone meal, submicron cigarette smoke, submicron aerosol crystals of NaCl, CsCl, KCl, NaI, NaCN, etc. Aperture 11 was a pinhole from 0.001 to 0.010 inch in diameter. Chamber 12 was maintained at 50–200 microns of mercury pressure by a mechanical vacuum pump and region 32 was maintained at 10^{-5} torr by a mercury diffusion pump. The heated surface 15 was composed of directly heated filaments comprising a metal, iridium (Ir), tungsten (W), tantalum (Ta), and platinum (Pt), as such, and also composed of such metals with a freshly deposited coating of tungsten by the pyrolytic decomposition of tungsten hexacarbonyl, $W(CO)_6$, by a known technique. Filament temperatures from 700°–2,000° C. were created by passing electric currents through the filaments. Successful results were also obtained by depositing and decomposing $W(CO)_6$ on nonconducting substrates such as quartz, glass or ceramic materials, such substrates being indirectly heated by an internal filament, or radition, or other appropriate techniques. Both the venetian blind type and box-and-grind type multipliers were used successfully. The preamplifier was a standard commercially available type with integrating time variable from $10^{-6}10^{-3}$ sec. The pulse-height analyzing devices used were the triggering level on an oscilloscope and a multichannel analyzer. Display instruments used were scalers and chart recorders. Inasmuch as aerodynamic forces are considerably stronger than gravitational forces for small particles, the entire apparatus may be mounted at any desired angle relative to the vertical.

In another embodiment shown in FIG. 3, an ion mass analyzing device 46 is inserted intermediate the heated surface 15 and the particle multiplier 36. Otherwise, in this as well as in subsequent embodiments, the same reference numerals are used for components similar to those used for describing FIG. 1. The mass analyzing device 46, which is shown here as a quadrupole mass filter, is powered through the set of feedthroughs 47 to which the mass analyzer power supply 50 is connected. In our laboratories, the mass analyzing device 46 consisted of a quadrupole mass filter. Using this device, we were able to ascertain that ion pulses of iodine, (I^-), chlorine (Cl^-), cyanogen (CN^-), bromine (Br^-), cesium (Cs^+), potassium (K^+), sodium (Na^+) and lithium (Li^+) were formed when and only when particles containing these components reached the heated surface. For example, aerosol crystals of CsCl, when impinged onto the heated surface, released bursts of Cs^+ and Cl^-, but not of the other aforementioned substances.

FIG. 4 illustrates a form of the invention wherein an additional chamber 51 is inserted for the purpose of providing a better vacuum in the region 32 of the detector apparatus. The intermediate chamber 51 is connected to an appropriate vacuum pump by means of a suitable vacuum connection to the opening 52. By causing most of the background gas to be pumped away through the opening 52, this technique allows a better vacuum in the region 32, permitting the use of devices such as quadrupole mass filters which require a vacuum better than 10^{-4} torr, and also permitting a larger initial aperture 11, reducing the tendency of the aperture 11 to become clogged.

FIG. 5 depicts a design of the apparatus similar to that in FIG. 4, except a means of tagging the particles with a specific substance is included. Thus the particles 10 pass through a small chamber 54 which contains a vapor of a specific surface-ionizable substance, for example, rubidium, said vapor being formed by heating a small sample 55 of the substance by means of a heating coil 56 surrounding the tagging chamber 54, with current being supplied to the coil through the set of

feedthroughs **57.** Although the tagging chamber is here shown in the intermediate chamber **51,** it could also be mounted in the lower chamber **32.**

For the case of cesium vapor heated to 100° C., it can be shown that the number of cesium atoms which strike a particle or radius r is $8 \times 10^2 r^2$, where r is given in microns. The actual number tagging the particle is the above number multipled by the sticking coefficient which, for a material such as cesium which exhibits strong chemisorption, should be nearly unity. In actual practice, it was found that this technique is effective only for large particles ($r > 10\mu$) because the cesium vapor also leaks out of the tagging chamber onto the filament, creating a large background signal.

FIG. **6** is a cross section of a different version of the tagging chamber. Here the problem of noise signals due to surface-ionizable vapor leaking out of the tagging chamber **54** onto the heated surface is reduced by using a cross-beam technique. A beam of the specific surface-ionizable substance, such as rubidium, is generated by heating the substance **55** within an oven **60** which is heated by a heating coil **61,** with current supplied to the coil through the set of feedthroughs **57.** The advantage of this technique is that the atoms or molecules of the specific surface-ionizable substance tend to leave the oven in a horizontal direction, where they can impinge upon and be trapped by a surface **62** which is cooled by contact with a coil of tubing **64** which contains a very cold liquid such as liquid nitrogen administered through an appropriate set of feedthrough conduits **65.** Such "cross-beam" tagging methods have been carried out in our laboratories, with the tagging atoms comprising cesium, rubidium, and lithium.

FIG. **7** is a cross-section of the uppermost portion of the apparatus illustrated in FIG. **4** including chamber **12.** However, prior to the pinhole **11** a set of vessels are provided for the purpose of adding to the surface of each particle **10,** while said particle suspended in a carrier gas, and prior to the injection of said particle into vacuum, a sufficient amount of surface-ionizable material so as to render the particle detectable by the apparatus of FIG. **4.** Particles **10** are thus passed slowly via an airstream through a tagging vessel **66** to which a vapor designated **67** is continually introduced through known techniques, the vapor **67** being comprised of atoms or molecules of a surface-ionizable substance, such as NaCl, Br_2, I_2, etc. Some of vapor **67** attaches to the surface of each particle **10,** the degree of attachment being dependent upon the size of the particle. Upon leaving the tagging vessel **66,** the particles are passed through a cleanup vessel **70** which contains a device (such as a cold surface) or a material (such as an appropriate chemical substance; for example, activated carbon for chlorine) which preferentially removes from the carrier gas most of those free tagging atoms (molecules) which have not been to the surface of a particle. Such chemical traps and cold traps are common to and easily within the skill of the art.

FIG. **8** represents one embodiment of the heated surface wherein the surface is composed of a conducting material, such as tungsten, which is directly heated by a current supplied by the surface power supply. In this design the surface **15** is a wire, or a coil of wire, or, preferably, a strip of a conducting material and is fastened to two support rods **71** which pass through the two vacuum-tight feedthroughs **61** mounted on the flange **35.**

FIG. **9** depicts another embodiment of the heated surface in which the surface is a conducting film **72** deposited on a non-conducting substrate **74** of arbitrary shape such as mica, quartz, ceramic, etc. Film **72** can be of any metal with suitable properties for surface-ionization, such as high work function, low vapor pressure, and chemical stability. Examples are tungsten, iridium and platinum. In order to maintain electrical contact with the film **72,** the apparatus is clamped onto a metallic block **75** of appropriate shape by means of a suitably designed metallic clamping device **78.** Block **75** is mounted onto an insulator **76** and a wire **77** fastened to the block **76** and to an electrical feedthrough **80** from a voltage source, selectively regulates the voltage on the thin film **72.** The entire assembly is mounted with insulating screws **81** on flange **35.** The substrate and thin film surface are heated by radiation from a filament **82** which is mounted on the two feedthroughs **16.** It is to be understood that this is one typical design out of several that have been constructed and out of many that could be constructed using the same principles. The advantage of this technique is that it is possible to make thin films of many metals which are considerably purer than commercially available wires and ribbons. Thin films of this type have been made of W, Pt, and Ir in these laboratories.

FIG. **10** represents a further embodiment of the heated surface in which two surfaces are used. In this design the particles to be detected are first pyrolized on one surface **84,** producing neutral atoms and molecules, some of which strike a nearby second surface **85** and are ionized. The first surface **84** is not necessarily a conducting material, in which case it will produce few or no ions of its own. Examples of suitable materials for surface **84** are quartz, glass and ceramic. Surface **84** can be constructed along similar lines as the apparatus described in FIG. **9.** For maximum efficiency, the second surface **85,** which can be directly or indirectly heated, is mounted parallel to the first, one such possible arrangement being shown in FIG. **10,** where the second surface **85** is directly heated and contains an aperture **86.** The particles are made to pass through the aperture and impinge upon the first surface **84,** where they are pyrolized and vaporized, thus producing a number of atoms and molecules, many of which strike the second surface **85,** some of these producing ions which can then be extracted from the intersurface region by suitable electric and magnetic fields and detected by the pulse-counting techniques discussed above. The advantages of such a technique are that one can use the optimum temperatures of dissociating a particle and for producing surface-ionization, (these temperatures generally not being the same), and that this technique can help avoid contamination of the ionizing surface.

FIG. **11** is an enlargement of an upper half of FIG. **1** wherein orifice **31** is replaced by a skimmer **87** of the type described by Anderson, Andres, and Fenn (Advances in Atomic and Molecular Physics **1,** 345 (1965)). This design is more effective for producing a beam of particles than that of FIG. **2,** especially for smaller particles, whereas for sufficiently heavy particles, the structure shown in FIG. **2** works just as well, is easier to construct, and is more rugged.

For the purposes of the claims "particle," as such, is intended to include (a) small particulate matter, whether electrically charged or neutral, whether solid or liquid, whether crystalline or polycrystalline, and of any chemical composition; or (b) large molecules of mass exceeding about 1,000 atomic mass units (AMU) with definite molecular structure, and polymers of such large molecules, whether in the free state or in a droplet or solvent, whether electrically charged or neutral and of any chemical nature. The work "ion," as such, shall include positively or negatively charged atoms, molecules, or radicals and shall also include, in the case of Claim 1, electrons.

What is claimed is:

1. A method of detecting a particle of dust, smoke and macromolecules of 1000 AMU or greater which comprises the steps of producing a burst of ions by inducing said particle to strike a heated surface and discerning the burst of ions so produced by the detection of its electrical charge.

2. A method in accordance with claim 1 wherein at least part of said burst of ions comprises surface-ionizable atoms or molecules occurring as constitutents of said particle including impurities therein.

3. A method in accordance with claim 1 wherein said particle is caused to pass through a vapor of surface-ionizable atoms or molecules prior to striking said heated surface, said surface-ionizable atoms or molecules attaching to said particle, at least part of said burst of ions comprising ions produced from said surface-ionizable atoms or molecules by surface ionization at the heated surface.

4. A method of determining the size of a particle of dust, smoke and other macromolecules of about 1,000 AMU or larger, of surface-ionizable atoms or molecules wherein some of said atoms or molecules are attached to said particle during its passage through the vapor in a number proportional to the size of said particle, causing said particle to strike a hot surface where said attached atoms or molecules are released and form a burst of ions, and detecting and measuring the electrical charge of said ions, the total amount of said electrical charge being proportional to the number of said attached surface-ionizable atoms or molecules and therefore indicative of the size of said particle.

5. An apparatus for the detection of individual gas-borne particles of dust, smoke and other macromolecules of 1,000 AMU or more which comprises ionization means which includes a heated surface in fluid communication with the gas containing and surrounding said particles, said surface adapted to receive said particles thereon and to produce a burst of ions through surface-ionization upon receiving one of said particles; and measuring means for performing the function of responding to the electric charge of said burst of ions including means for performing the function of registering said charge.

6. An apparatus in accordance with claim 5 wherein said measuring means includes a second surface, said heated surface and said second surface being at different potentials whereby an electric field is created between said surfaces which is adapted to cause a burst of ions produced at said heated surface to be accelerated to said second surface.

7. An apparatus in accordance with claim 5, comprising means for creating an electric field wherein said heated surface is located in said electric field, said electric field being of such an intensity that the production of burst of ions at the heated surface initiates electrical breakdown of the carrier gas, said breakdown producing an additional number of ions, said ions being detected by said means.

8. An apparatus in accordance with claim 5 wherein said heated surface is located in a cylinder through which the gas containing and surrounding the particles, means being associated with said cylinder for inducing said gas to move at a speed sufficiently high that said particles are impact with high efficiency onto said heated surface.

9. An apparatus in accordance with claim 8 comprising means for creating an electric field wherein said heated surface is located in said electrical field, said electrical field being of such an intensity that the production of burst of ions at the heated surface initiates electrical breakdown of the carrier gas, said breakdown producing an additional number of ions, said ions being detected by said means.

10. An apparatus in accordance with claim 5 wherein said measuring means comprises a pulse height discriminator adapted to separate small pulses caused by surface-ionizable impurities in the material of the heated surface from more intense pulses caused by said ions produced at said heated surface upon being struck by said particles.

11. An apparatus in accordance with claim 5 wherein said heated surface is composed of a metal in the group consisting of tungsten, iridium, platinum, tantalum, molybdenum, rhenium and gold.

12. An apparatus in accordance with claim 5 wherein a circuit is provided for passing current through said heated surface for causing it to become heated.

13. An apparatus in accordance with claim 5, wherein a further heated surface is included which is adapted to pyrolize said particles thereby producing surface-ionizable atoms, molecules or radicals which thereafter strike said first-mentioned heated surface, where some of said atoms, molecules or radicals become surface-ionized, said ions being detected by said registration means.

14. An apparatus in accordance with claim 13 wherein the temperature of said first-heated surface is higher than the temperature of said further heated surface.

15. An apparatus for the detection of particles of dust, smoke and other macromolecules of 1,000 AMU or more which comprises a vacuum chamber with a small aperture opening to the gas containing and surrounding said particles, means for continuously exhausting said vacuum chamber, the capacity of said exhaust means and the size of said small aperture being such that the chamber is maintained at a pressure substantially less than atmospheric pressure, a heated surface within said vacuum chamber located to receive particles therein and adapted to produce a burst of ions upon being struck by one of said particles in said vacuum chamber, and measuring means for performing the function of registering said bursts of ions produced at said heated surface.

16. An apparatus in accordance with claim 15 wherein said measuring means includes an electron multiplier.

17. An apparatus in accordance with claim 15 wherein said measuring means comprises a pulse height discriminator adapted to separate small pulses caused

by surface-ionizable impurities in the material of the heated surface from more intense pulses caused by said burst of ions produced at said heated surface upon being struck by said particles.

18. An apparatus in accordance with claim 15 wherein a further heated surface is included which is adapted to pyrolize said particles thereby producing surface-ionizable atoms, molecules or radicals which thereafter strike said first-mentioned heated surface, where some of said atoms, molecules or radicals become surface-ionized, said ions being detected by said registration means.

19. An apparatus in accordance with claim 18 wherein the temperature of said first-heated surface is higher than the temperature of said further heated surface.

20. An apparatus in accordance with claim 15 wherein a circuit is provided for passing current through said heated surface for causing it to become heated.

21. An apparatus in accordance with claim 15, wherein said heated surface is composed of a metal in the group consisting of tungsten iridium, platinum, tantalum, molybdenum, rhenium and gold.

22. An apparatus in accordance with claim 15 wherein said measuring means includes means for separating ions according to their charge-to-mass ratio.

23. An apparatus in accordance with claim 22, wherein said means for separating ions according to their charge-to-mass ratio is a quadrupole mass filter.

24. An apparatus for the detection of particles of dust, smoke and other macromolecules of 1,000 AMU or more which comprises a first vacuum chamber with a small aperture opening to the gas containing and surrounding said particles and a small opening to a second vacuum chamber, said aperture and said opening being aligned, means for continuously exhausting both said vacuum chambers in a differential pumping arrangement, the capacity of said exhaust means and the sizes of said aperture and said opening being such that said first vacuum chamber is maintained at a pressure substantially less than atmospheric pressure and that said second vacuum chamber is maintained at a pressure substantially less than the pressure in said first vacuum chamber, a heated surface within said second vacuum chamber located to receive particles that pass in a substantially straight line through said aperture and said opening and enter the second chamber, said surface being adapted to produce a burst of ions upon being struck by one of said particles, and measuring means responsive to said burst of ions including means for registering burst of ions produced at said heated surface.

25. An apparatus in accordance with claim 24 wherein a circuit is provided for passing current through said heated surface for causing it to become heated.

26. An apparatus in accordance with claim 24 wherein said measuring means comprises a pluse height discriminator adapted to separate small pulses caused by surface-ionizable impurities in the material of the heated surface from more intense pulses caused by said burst of ions produced at said heated surface upon being struck by one of said particles.

27. An apparatus in accordance with claim 24 wherein said heated surface is composed of a metal in the group consisting of tungsten, iridium, platinum, tantalum, molybdenum, rhenium and gold.

28. An apparatus in accordance with claim 24 wherein said measuring means includes an electron multiplier.

29. An apparatus according to claim 24 wherein one of the vacuum chambers other than said second vacuum chamber contains means for producing therein a vapor of surface-ionizable atoms or molecules.

30. An apparatus in accordance with claim 29 wherein said vapor is composed of an organic compound from which positive ions of organic radicals or the negative ion CN^- is produced by surface-ionization.

31. An apparatus in accordance with claim 29 wherein said vapor is composed of an alkali metal in the group consisting of lithium, sodium, potassium, rubidium and cesium.

32. An apparatus in accordance with claim 29 wherein said vapor is composed of a compound containing halogen atoms in the group consisting of fluorine, chlorine, bromine and iodine, or molecules in the group consisting of fluorine, chlorine, bromine and iodine.

33. An apparatus in accordance with claim 29 including means for producing said vapor in the form of an atomic or molecular beam across which said particles must pass.

34. An apparatus in accordance with claim 24 wherein a further heated surface is included which is adapted to pyrolize said particles producing surface-ionizable atoms, molecules or radicals which thereafter strike first-mentioned heated surface, where some of said atoms, molecules or radicals become surface-ionized, said ions being detected by said registration means.

35. An apparatus in accordance with claim 34 wherein the temperature of said first-heated surface is higher than the temperature of said further heated surface.

36. An apparatus in accordance with claim 24 wherein said measuring means includes means for separating ions according to their charge-to-mass ratio.

37. An apparatus in accordance with claim 36 wherein said means for separating ions according to their charge-to-mass ratio is a quadrupole mass filter.

38. An apparatus in accordance with claim 24 in which one or more vacuum chambers and means for exhausting said vacuum chambers are placed intermediate between said first vacuum chamber and said second vacuum chambers, in a differential pumping arrangement.

39. An apparatus in accordance with claim 38 wherein said measuring means comprises a pulse height discriminator adapted to separate small pulses caused by surface-ionizable impurities in the material of the heated surface from more intense pulses caused by said burst of ions produced at said heated surface upon being struck by one of said particles.

40. An apparatus in accordance with claim 38 wherein said heated surface is composed of a metal in the group consisting of tungsten, iridium, platinum, tantalum, molybdenum, rhenium and gold.

41. An apparatus in accordance with claim 38 wherein a circuit is provided for passing current

through said heated surface for causing it to become heated.

42. An apparatus in accordance with claim **38** wherein said measuring means includes an electron multiplier.

43. An apparatus in accordance with claim **38** wherein a further heated surface is included which is adapted to pyrolize said particles thereby producing surface-ionizable atoms, molecules or radicals which thereafter strike said first-mentioned heated surface, where some of said atoms, molecules or radicals become surface-ionized, said ions being detected by said registration means.

44. An apparatus in accordance with claim **43** wherein the temperature of said first-heated surface is higher than the temperature of said further heated surface.

45. An apparatus in accordance with claim **38** wherein said measuring means includes means for separating ions according to their charge-to-mass ratio.

46. An apparatus in accordance with claim **45** wherein said means for separating ions according to their charge-to-mass ratio is a quadrupole mass filter.

47. An apparatus in accordance with claim **38** wherein one of the vacuum chambers other than said second vacuum chamber contains means for producing therein a vapor of surface-ionizable atoms or molecules.

48. An apparatus in accordance with claim **47**, wherein said vapor is composed of an organic compound from which positive ions of organic radicals or the negative ion CN^- is produced by surface-ionization.

49. An apparatus in accordance with claim **47** including means for producing said vapor in the form of an atomic or molecular beam across which said particles must pass.

50. An apparatus in accordance with claim **47** wherein said vapor is composed of molecules or compounds containing halogen atoms in the group consisting of fluorine, chlorine, bromine and iodine, or molecules of the group consisting of fluorine, chlorine, bromine, and iodine.

51. An apparatus in accordance with claim **47** wherein said vapor is composed of an alkali metal in the group consisting of lithium, sodium, potassium, rubidium and cesium.

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