



(22) Date de dépôt/Filing Date: 2016/07/25

(41) Mise à la disp. pub./Open to Public Insp.: 2018/01/25

(51) Cl.Int./Int.Cl. *H01J 49/16* (2006.01),
H01J 49/04 (2006.01), *H01J 49/26* (2006.01)

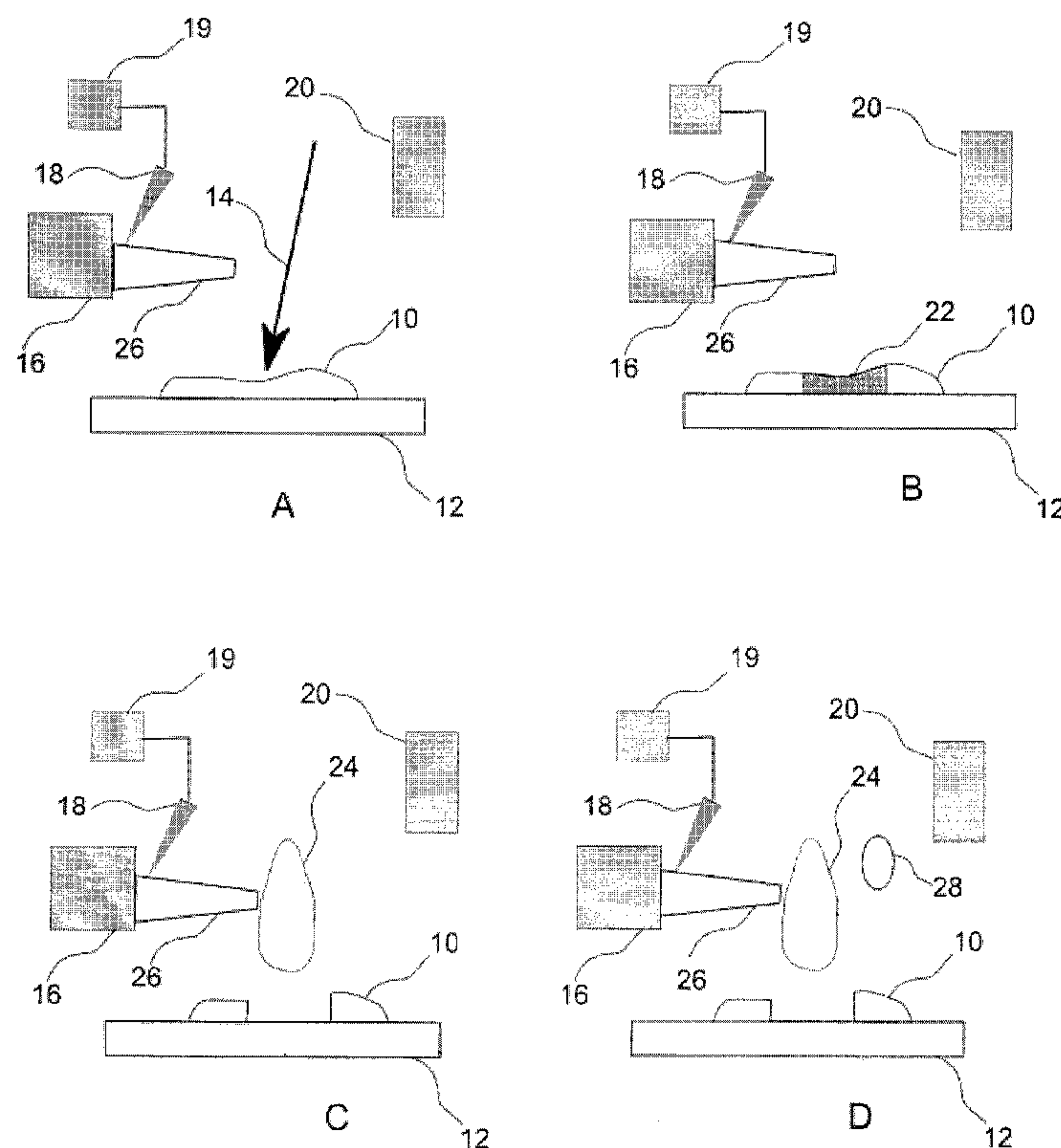
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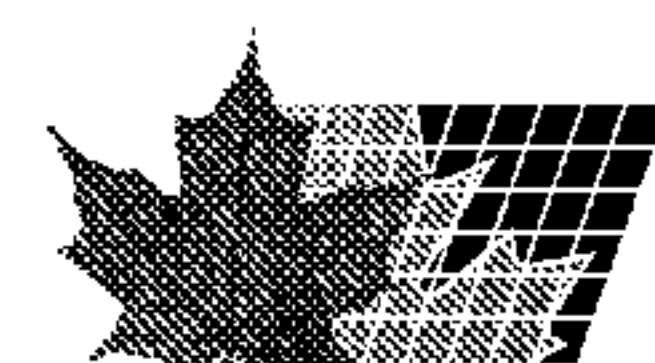
(54) Titre : METHODES D'IONISATION DE PANACHES LASER PAR IONISATION CHIMIQUE A PRESSION
ATMOSPHERIQUE

(54) Title: METHOD FOR IONIZING LASER PLUMES THROUGH ATMOSPHERIC PRESSURE CHEMICAL IONIZATION



(57) Abrégé/Abstract:

Method for ionizing laser plumes using atmospheric pressure chemical ionization (APCI) is disclosed. A laser plume is ionized by intercepting it with an ionized gas jet where said ionized jet contains dopant molecules that are previously ionized through atmospheric pressure chemical ionization (APCI) process.



Title:

Method for ionizing laser plumes through atmospheric pressure chemical ionization

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ABSTRACT

Method for ionizing laser plumes using atmospheric pressure chemical ionization (APCI) is disclosed. A laser plumes is ionized by intercepting it with an ionized gas jet where said ionized jet contains dopant molecules that are previously ionized through atmospheric pressure chemical ionization (APCI) process.

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Background

Mass spectrometry is one of the most important diagnostic techniques for determining molecular composition of a sample. In case of samples in condensed phase, several processing steps are required for mass spectrometry analysis:

- (a) desorption of sample molecules i.e. moving sample molecules from the condensed into the gas phase;
- (b) ionization of the desorbed molecules;
- (c) coupling such ionized sample molecules into a mass spectrometer.

In case of fragile molecules, such as majority of biological molecules, the first two steps involving desorption and ionization are critical since desorption and ionization processes are generally energy intensive; so it is easy to put excess energy into the sample molecules which can cause their modification or break-up. Recent advances in laser ablation techniques, which desorb molecules through creation of laser ablation plumes, make possible desorption with imparting minimal excess energy into desorbed sample molecules; however, the most optimal ionization method of such desorbed molecules is still to be determined.

One of the standard methods for ionizing gas phase molecules is atmospheric pressure chemical ionization (APCI) which consists of putting a sharp metal object under high voltage in the vicinity of sample molecules which are desorbed in a gas atmosphere. Such sharp metal object creates corona discharge which generates charges that are transferred to the sample molecules either directly or indirectly through interactions with molecules in the gas atmosphere of liquid sample matrix molecules (e.g. water or alcohol) that are desorbed simultaneously with the sample molecules. APCI is a standard ionization technique and its general features are known to the person having ordinary skill in the art.

However, a standard APCI configuration is not an efficient method for ionizing laser plumes since laser plumes are highly localized in space and time while standard APCI corona discharges are not.

For that reason, an APCI method that that delivers ions co-localized with gas phase sample molecules in time and space would be advantageous.

Description

Referring to FIGS. 1A-1D, a sample **10** in the condensed phase is deposited on a sample holder **12**. A laser pulse **14** is directed at sample **10** where the laser pulse is absorbed thus creating a superheated portion of said sample. The superheated portion gets ablated creating a laser plume **24** that is generally

an aerosol consisting of gas phase sample molecules, gas phase matrix molecules, molecular aggregates, small sample droplets, etc. A source **16** that creates a gas jet **26** is placed in the vicinity of said sample where said gas jet contains dopant molecules. Close to the outlet of said gas jet there is a sharp metal object **18** that is in electrical contact with a high voltage source **19**. Due to the high voltage at the sharp tip of said sharp metal object, a corona discharge is formed ionizing some of the dopant molecules within said laser jet. Such ionized dopant molecules travel with jet **26** which is directed in a way to intercept laser plume **24**. Some of these ionized dopant molecules transfer their charges to some of the sample molecules of interest within laser plume **24**. Such ionized sample molecules form a cloud **28** which is directed towards a mass spectrometer **20** where these sample molecules are analyzed.

Referring to FIG. 2A, the schematic shows an example of gas jet source **16** presented in Fig. 1. A pressured gas source (for example a gas cylinder or a compressor) **34** delivers a gas to a thin capillary **30** through a tubing **32**. The gas passes through the capillary and exits at one of its ends creating a gas jet **26** corresponding to gas jet **26** from FIG. 1. Gas jet **26** is partially or completely ionized by a corona discharge created by sharp metal object **18** that is at high voltage provided by high voltage generator **19**. High voltage generator **19** can provide constant high voltage or it can be modulated or pulsed in which case the frequency and phase of such modulation or pulsing should be synchronized to the ablative laser pulse in order to provide the optimal number of ions to the laser plume.

FIG. 2B shows a possible variation of the system schematically presented in FIG 2A. In this case, sharp metal object **18** from FIG 2A has a form of a long needle **36** inserted inside capillary **30** where the sharp tip of needle **36** is positioned close to the capillary end where the gas exists forming gas jet **26**. Needle **36** is at high voltage provided by high voltage generator **19** thus creates a corona discharge that partially or completely ionizes gas jet **26**.

FIG. 3A shows a simple schematic of mass spectrometer **20** from FIG 1. Mass spectrometer **20** has an orifice that is the entrance point for ions into mass spectrometer. Features and design principles of mass spectrometers and their orifices are known to the person having ordinary skill in the art.

FIG. 3A shows a simple schematic of a system presented in FIG 3A with an added feature **54** that corresponds to a system that provides static or/and dynamic electromagnetic fields that help guiding the ion cloud **28** into mass spectrometer **50**. Features and design principles of such electromagnetic systems are known to the person having ordinary skill in the art.

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Claims:

1. A mass spectrometry system for analyzing molecular composition of a sample in a condensed phase comprising:

a pulsed laser capable of ablating the surface of said sample in a region where atmospheric pressure thus creating an ablation plume containing analyte molecules;

a system for delivering a gas jet where said gas jet contains dopant molecules;

a metal object with a sharp tip placed in the vicinity of said gas jet;

a high voltage generator that is electrically connected to said metal object, thus creating a corona discharge at said sharp tip, where said corona discharge ionizes said dopant molecules in said gas jet;

and where said gas jet intercepts said laser ablation plume whereby at least one of subsequent direct or indirect collisions between said ionized dopant molecules and said analyte molecules results in ionization of several said analyte molecules;

and where said ionized analyte molecules are directed towards a mass spectrometer where said ionized analyte molecules are analyzed providing information about molecular composition of said sample.

2. A system described in Claim 1 where said system for delivering gas jet is a capillary connected with a tubing to a source of compressed gas.

3. A system described in Claim 2 where said source of compressed gas is a gas cylinder or gas compressor.

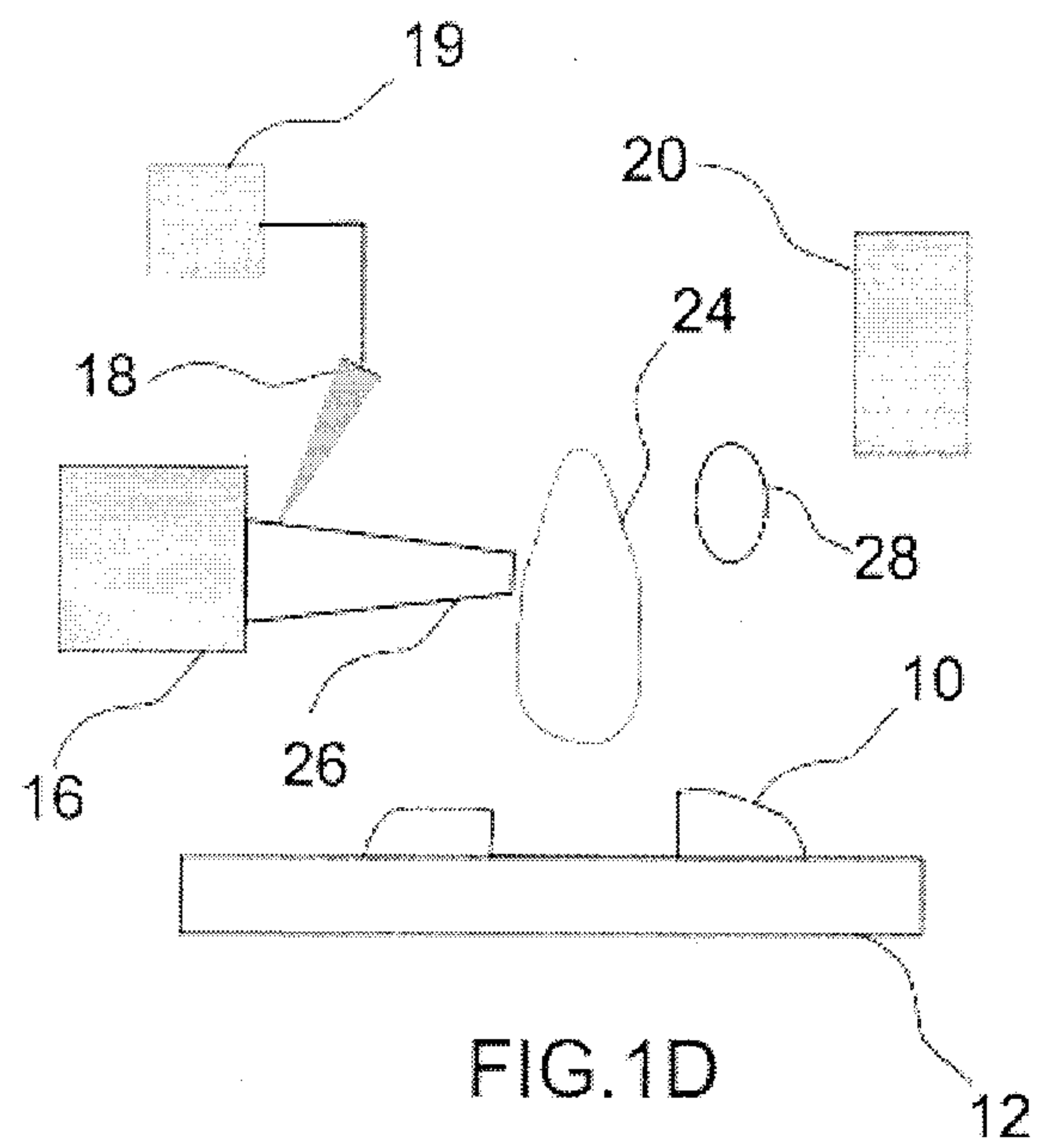
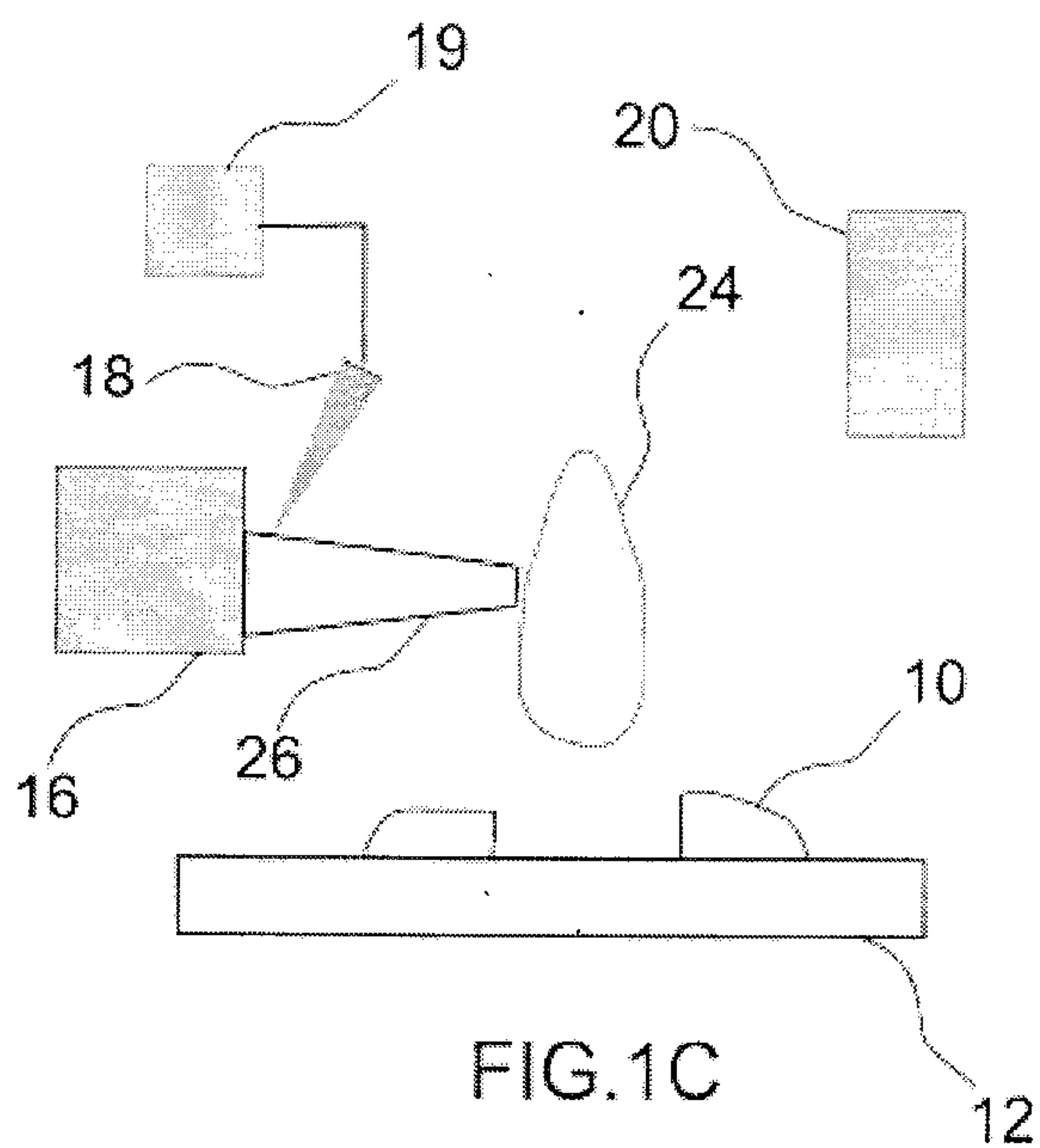
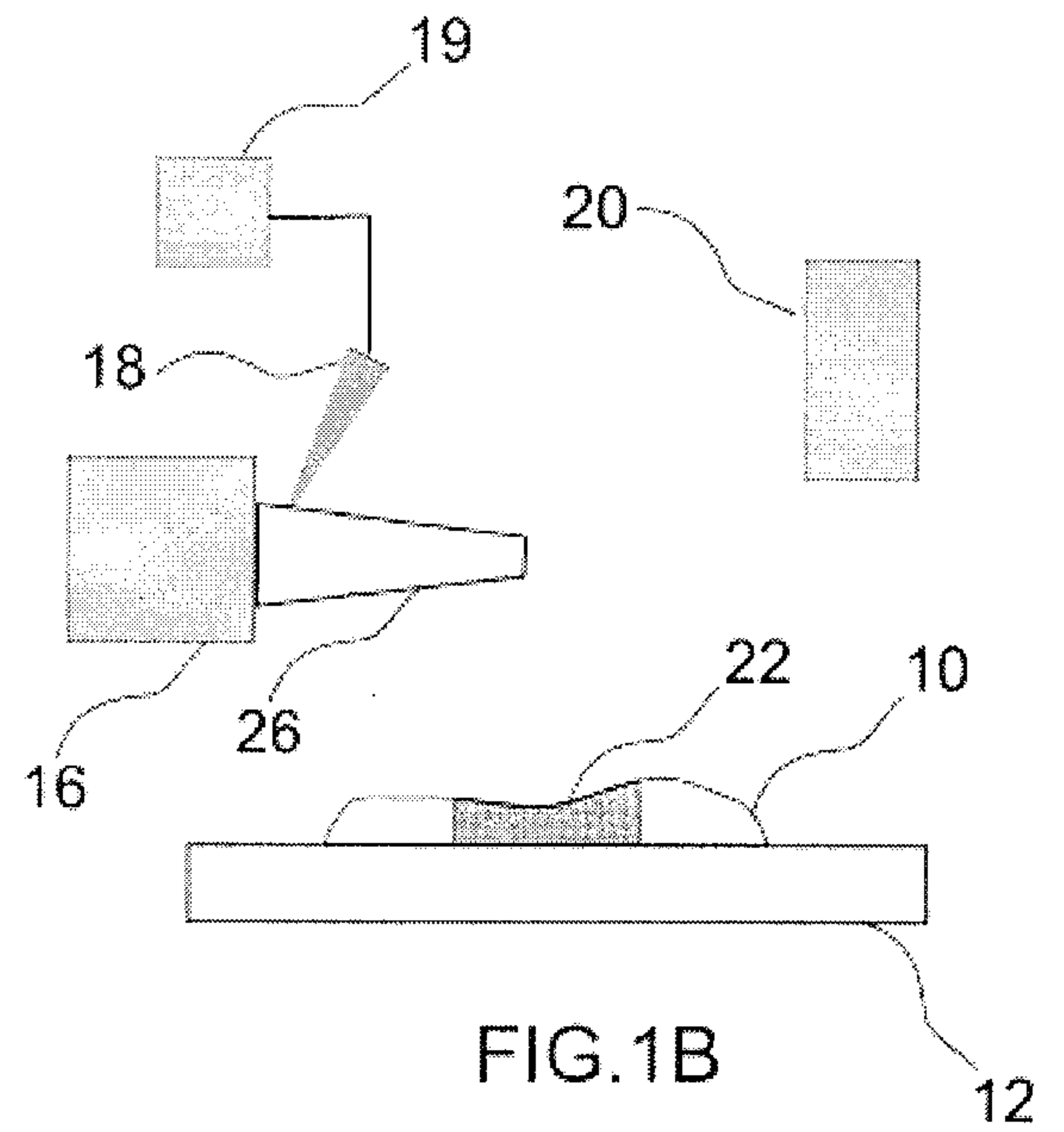
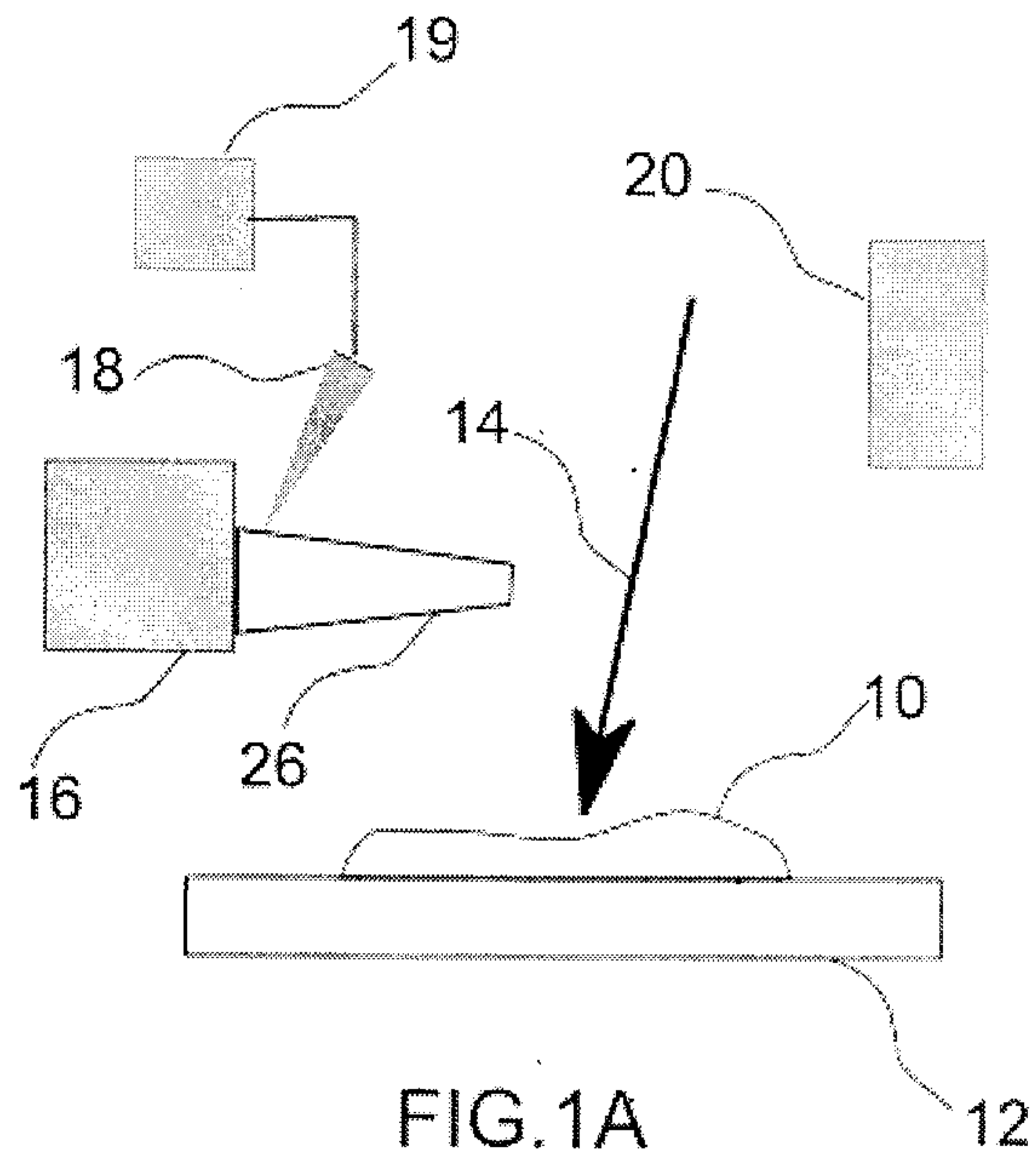
4. A system described in Claims 2 and 3 where said metal object with a sharp tip has a form of a sharp needle that is placed within said capillary.

5. A system described in Claims 1,2,3, and 4 where said gas contains air, water vapour, N₂, noble gas, toluene, or a mixture of any of these gases.

6. A system described in Claims 1,2,3,4, and 5 where said high voltage source is pulsed, modulated, or constant.

7. A system described in Claim 1 where said system for delivering a gas jet has a pulsed valve.

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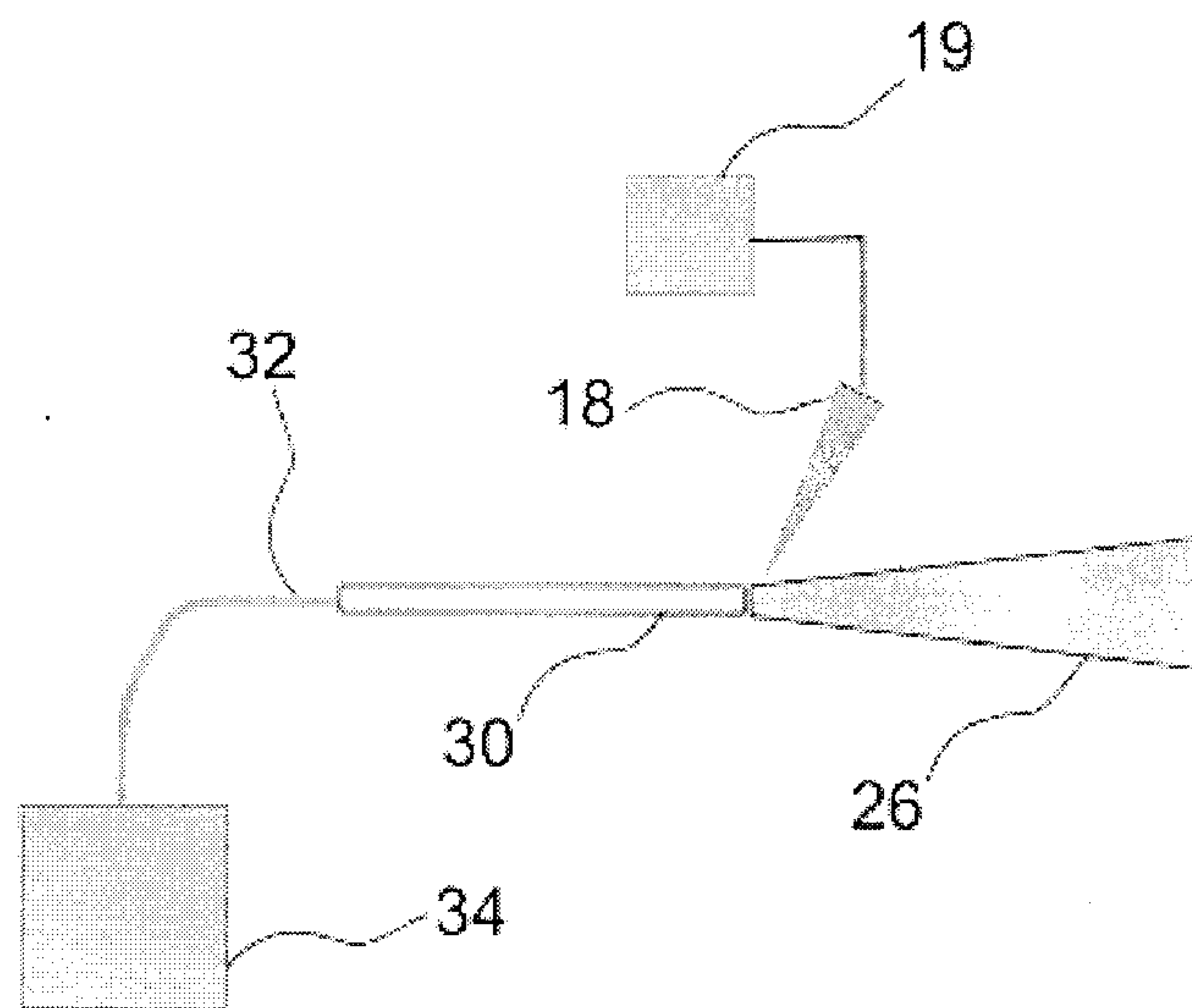


FIG. 2A

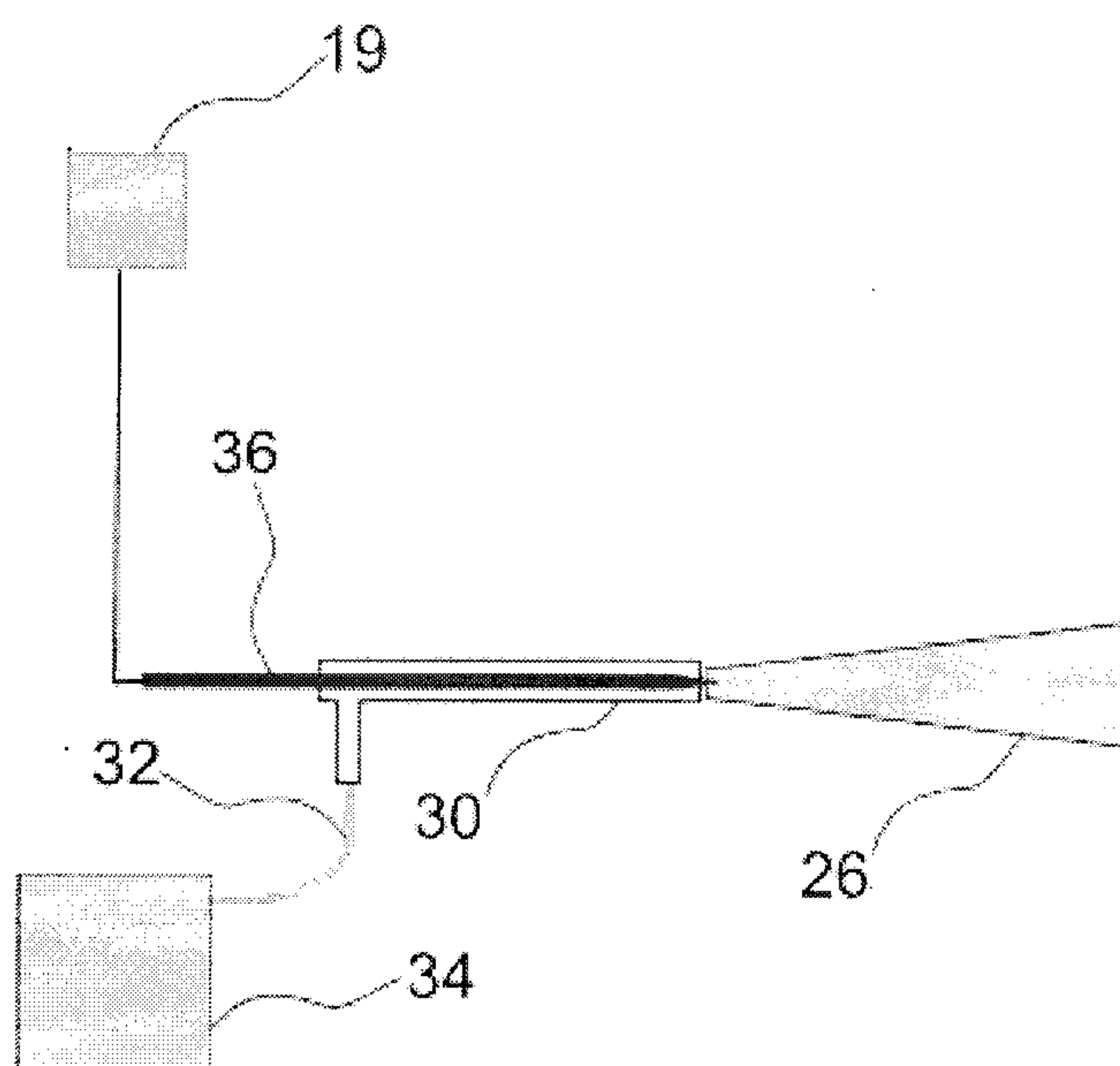


FIG. 2B

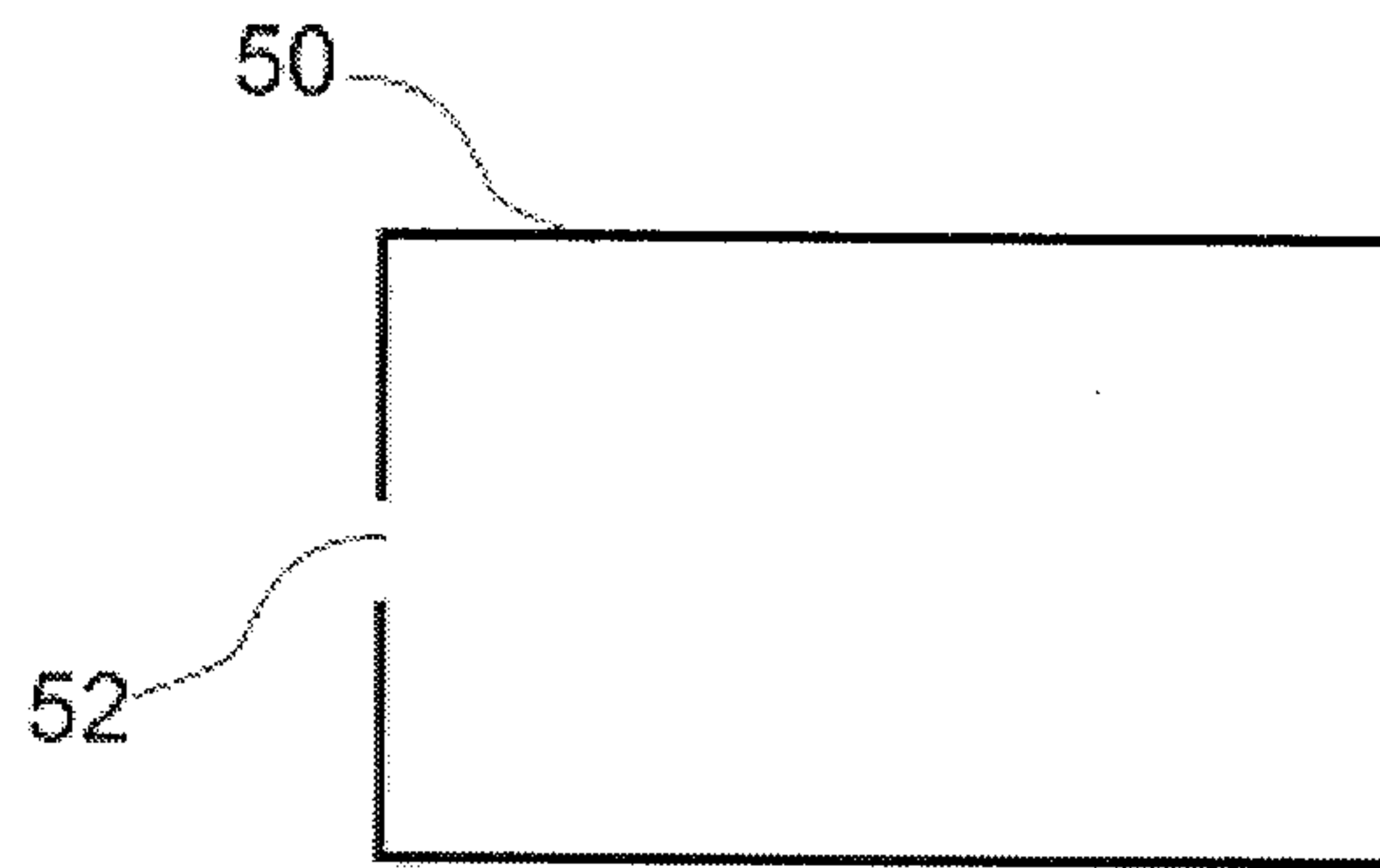


FIG. 3A

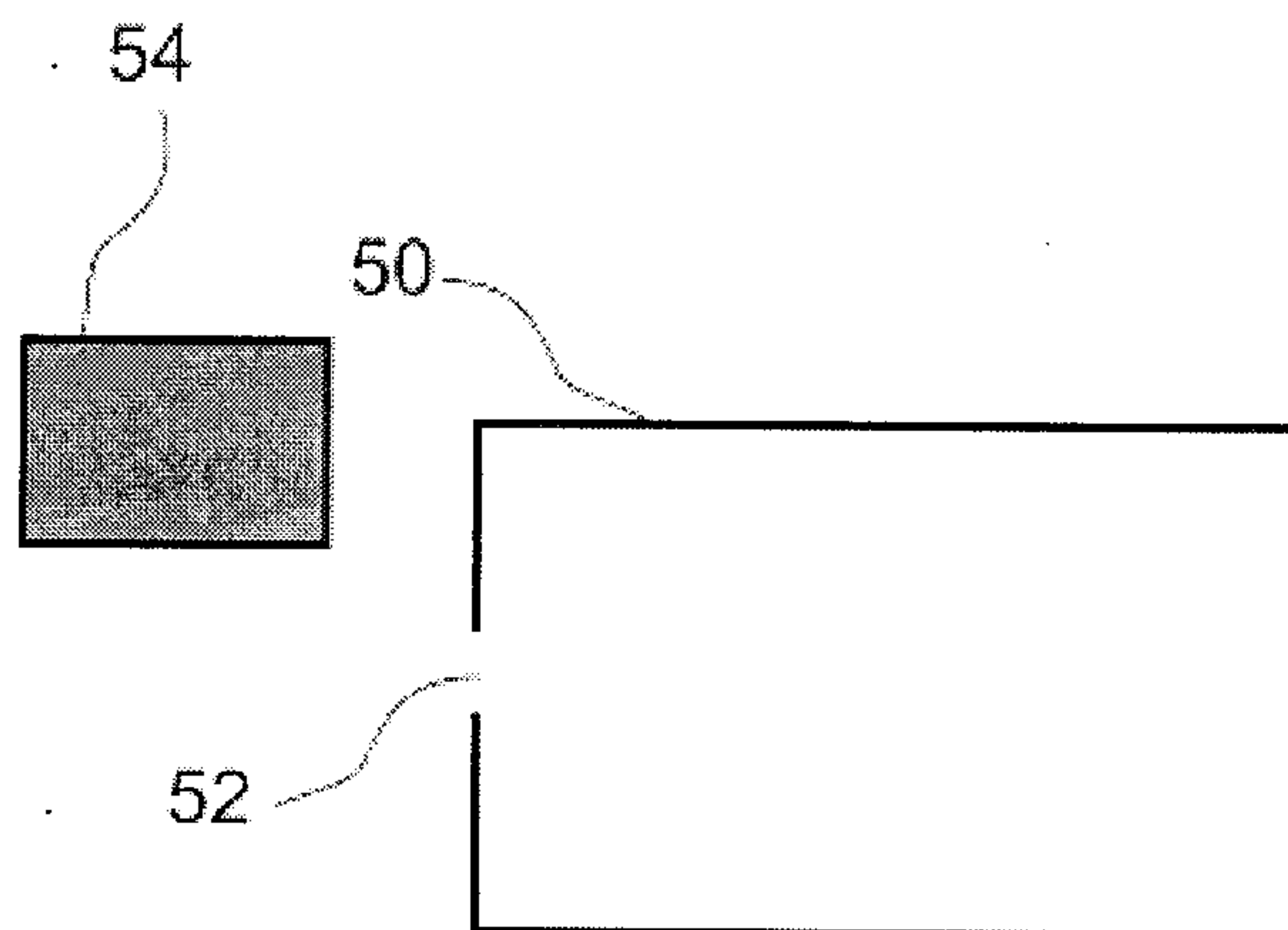


FIG. 3B

