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(54) Titre : PREPARATIONS CATALYSANTES DE RUTHENIUM-COBALT EXEMPTES DE PLATINE DESTINEES A LA
PRODUCTION D'HYDROGENE
(54) Title: PLATINUM-FREE RUTHENIUM-COBALT CATALYST FORMULATIONS FOR HYDROGEN GENERATION

(57) **Abrégé/Abstract:**

A method and catalysts and fuel processing apparatus for producing a hydrogen-rich gas, such as a hydrogen-rich syngas are disclosed. According to the method, a CO-containing gas, such as a syngas, contacts a platinum-free ruthenium-cobalt water gas shift ("WGS") catalyst, in the presence of water and preferably at a temperature of less than about 450°C., to produce a hydrogen-rich gas, such as a hydrogen-rich syngas. Also disclosed is a platinum-free ruthenium-cobalt water gas shift catalyst formulated from: a) Ru, its oxides or mixtures thereof, b) Co, Mo, their oxides or mixtures thereof, and c) at least one of Li, Na, K, Rb, Cs, Ti, Zr, Cr, Fe, La, Ce, Eu, their oxides and mixtures thereof. The WGS catalyst may be supported by a carrier, such as any one member or a combination of alumina, zirconia, titania, ceria, magnesia, lanthania, niobia, zeolite, perovskite, silica clay, yttria and iron oxide. Fuel processors containing such water gas shift catalysts are also disclosed.



ABSTRACT

A method and catalysts and fuel processing apparatus for producing a hydrogen-rich gas, such as a hydrogen-rich syngas are disclosed. According to the method, a CO-containing gas, such as a syngas, contacts a platinum-free ruthenium-cobalt water gas shift ("WGS") catalyst, in the presence of water and preferably at a temperature of less than about 450°C., to produce a hydrogen-rich gas, such as a hydrogen-rich syngas. Also disclosed is a platinum-free ruthenium-cobalt water gas shift catalyst formulated from: a) Ru, its oxides or mixtures thereof, b) Co, Mo, their oxides or mixtures thereof, and c) at least one of Li, Na, K, Rb, Cs, Ti, Zr, Cr, Fe, La, Ce, Eu, their oxides and mixtures thereof. The WGS catalyst may be supported by a carrier, such as any one member or a combination of alumina, zirconia, titania, ceria, magnesia, lanthania, niobia, zeolite, perovskite, silica clay, yttria and iron oxide. Fuel processors containing such water gas shift catalysts are also disclosed.

PLATINUM-FREE RUTHENIUM-COBALT CATALYST FORMULATIONS FOR HYDROGEN GENERATION

BACKGROUND OF THE INVENTION

Field of the Invention

The invention relates to methods and catalysts for generating a hydrogen-rich gas from gas mixtures containing carbon monoxide and water, such as water-containing
15 syngas mixtures. More particularly, the invention includes methods using platinum-free catalysts which contain ruthenium and cobalt, and ruthenium, cobalt and molybdenum. The catalysts may be supported on a variety of catalyst support materials. The ruthenium-cobalt catalysts of the invention exhibit both high activity and selectivity to hydrogen generation and carbon monoxide oxidation.

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Discussion of the Related Art

Numerous chemical and energy-producing processes require a hydrogen-rich composition (*e.g.* feed stream.) A hydrogen-rich feed stream is typically combined with other reactants to carry out various processes. Nitrogen fixation processes, for example,
25 produce ammonia by reacting feed streams containing hydrogen and nitrogen under high pressures and temperatures in the presence of a catalyst. Fuel cells such as polymer electrode membrane ("PEM") fuel cells, produce energy from a hydrogen-rich feed stream. PEM fuel cells typically operate with a feedstream gas inlet temperature of less than 450 °C. Carbon monoxide is excluded from the feed stream to the extent possible to
30 prevent poisoning of the electrode catalyst, which is typically a platinum-containing catalyst. See U.S. Patent No. 6,299,995.

One route for producing a hydrogen-rich gas is hydrocarbon steam reforming. In a hydrocarbon steam reforming process steam is reacted with a hydrocarbon fuel, such as methane, iso-octane, toluene, *etc.*, to produce hydrogen gas and carbon dioxide. The reaction, shown below with methane (CH₄), is strongly endothermic:

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In the petrochemical industry, hydrocarbon steam reforming of natural gas is typically performed at temperatures in excess of 900°C. Even for catalyst assisted hydrocarbon steam reforming the temperature requirement is often still above 700 °C. See, for example, U.S. Patent No. 6,303,098. Steam reforming of hydrocarbons such as methane, using nickel- and gold-containing catalysts and temperatures greater than 450 °C, is described in U.S. Patent No. 5,997,835. The catalyzed process forms a hydrogen-rich gas, with depressed carbon formation.

One example of effective hydrocarbon steam reforming catalysts is the Sinfelt compositions which are composed of Pt, a Group 11 metal, and a Group 8 to 10 metal. Group 11 metals include Cu, Ag and Au while Group 8 to 10 metals include the other noble metals. These catalyst formulations are well known in the promotion of hydrogenation, hydrogenolysis, hydrocracking, dealkylation of aromatics, and naphtha reforming processes. See, for example, U.S. Patent Nos. 3,567,625 and 3,953,368. The application of catalysts based on the Sinfelt model to the water gas shift ("WGS") reaction, in particular at conditions suitable for lower temperature WGS applications such as PEM fuel cells, has not been previously reported.

Purified hydrogen-containing feed streams have also been produced by filtering the gas mixture produced by hydrocarbon steam reformation through hydrogen-permeable and hydrogen-selective membranes. See, for example, U.S. Patent No. 6,221,117. Such approaches suffer from drawbacks due to the complexity of the system and slow flow rates through the membranes.

Another method of producing a hydrogen-rich gas such as a feed stream starts with a gas mixture containing hydrogen and carbon monoxide with the absence of any substantial amount of water. The carbon monoxide can be removed by absorption and/or

by its oxidation to carbon dioxide. Such a process utilizing a ruthenium based catalyst to remove and oxidize the carbon monoxide is disclosed in U.S. Patent No. 6,190,430.

The WGS reaction provides another mechanism for producing a hydrogen-rich gas but from water (steam) and carbon monoxide. An equilibrium process, the water gas shift
5 reaction, shown below, converts water and carbon monoxide to hydrogen and carbon dioxide, and vice versa.



Various catalysts have been developed to catalyze the WGS reaction. These catalysts are typically intended for use at temperatures greater than 450 °C and/or pressures above 1
10 bar. For instance, U.S. Patent No. 5,030,440 relates to a palladium and platinum-containing catalyst formulation for catalyzing the shift reaction at 550 to 650°C. See also U.S. Patent No. 5,830,425 for an iron/copper based catalyst formulation.

Catalytic conversion of water and carbon monoxide under water gas shift reaction conditions has historically been used to produce hydrogen-rich and carbon monoxide-poor
15 gas mixtures. Existing WGS catalysts, however, do not exhibit sufficient activity at a given temperature to reach or even closely approach thermodynamic equilibrium concentrations of hydrogen and carbon monoxide such that the product gas may subsequently be used as a hydrogen feed stream. Specifically, existing catalyst formulations are not sufficiently active at low temperatures, *i.e.* temperatures below about
20 450 °C. See U.S. Patent No. 5,030,440.

Platinum (Pt) is a well-known catalyst for both hydrocarbon steam reforming and water gas shift reactions. Under the typical hydrocarbon steam reforming conditions of high temperature (above 850 °C) and high pressure (greater than 10 bar), the WGS reaction may occur post-reforming over the hydrocarbon steam reforming catalyst due to
25 the high temperature and generally unselective catalyst compositions. See, for instance, U.S. Patent Nos. 6,254,807; 5,368,835; 5,134,109 and 5,030,440 for a variety of catalyst compositions and reaction conditions under which the water gas shift reaction may occur post-reforming. A drawback to the use of Pt in catalyst compositions is its expense.

Metals such as cobalt (Co), ruthenium (Ru), palladium (Pd), rhodium (Rh) and
30 nickel (Ni) have also been used as WGS catalysts but are normally too active for the selective WGS reaction and cause methanation of CO to CH₄ under typical reaction

conditions. In other words, the hydrogen produced by the water gas shift reaction combines with CO in the presence of WGS catalysts to yield methane. This tendency toward methanation has typically limited the utility of metals such as Co, Ru, Pd, Rh and Ni as water gas shift catalysts.

5 A need exists, therefore, for a method of producing a hydrogen-rich syngas using relatively inexpensive platinum-free catalysts which are highly active and highly selective for both hydrogen generation and carbon monoxide oxidation at moderate temperatures (*i.e.* below about 450 °C) to provide a hydrogen-rich gas, such as a hydrogen-rich syngas, from a gas mixture containing, at least CO, and preferably hydrogen.

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SUMMARY OF THE INVENTION

The invention meets the need for highly active and selective platinum-free ruthenium-cobalt catalysts for the generation of hydrogen and the oxidation of carbon monoxide and to thereby provide a hydrogen-rich gas, such as a hydrogen-rich syngas, from a gas mixture of at least carbon monoxide and water. Accordingly, the invention provides methods and catalysts for producing a hydrogen-rich gas.

15 The invention is, in a first general embodiment, a method for producing a hydrogen-rich gas (e.g., syngas) by contacting a CO-containing gas, such as a syngas mixture, with a platinum-free water gas shift catalyst in the presence of water at a temperature of not more than 450°C. In the first general embodiment, the water gas shift catalyst, with an essential absence of Pt, comprises (a) Ru, its oxides or mixtures thereof; (b) Co, Mo, their oxides or mixtures thereof; and (c) at least one of Li, Na, K, Rb, Cs, Ti, Zr, Cr, Fe, La, Ce, Eu, their oxides and mixtures thereof. The catalyst may be supported on a carrier, for example, at least one member selected from the group consisting of alumina, zirconia, titania, ceria, magnesia, lanthania, niobia, zeolite, perovskite, silica clay, yttria, iron oxide and mixtures thereof. The method of the invention may be conducted at a temperature ranging from about 150 °C to about 450 °C.

25 In a second general embodiment, the invention relates to the water gas shift catalysts themselves – both supported and unsupported catalysts. In a more particularized first embodiment, the inventive water gas shift catalyst, with an essential absence of Pt, comprises (a) Ru, its oxides or mixtures thereof; (b) Co, Mo, their oxides or mixtures

thereof; and (c) at least one of Li, Na, K, Rb, Cs, Ti, Zr, Cr, Fe, La, Ce, Eu, their oxides and mixtures thereof. The catalyst may be supported on a carrier comprising at least one member selected from the group consisting of alumina, zirconia, titania, ceria, magnesia, lanthania, niobia, zeolite, perovskite, silica clay, yttria and iron oxide.

5 In a third general embodiment, the invention is directed to the aforementioned water gas shift catalysts of the second general embodiment in an apparatus for generating a hydrogen gas containing stream from a hydrocarbon or substituted hydrocarbon feed stream. The apparatus further comprises, in addition to the WGS catalyst, a fuel reformer, a water gas shift reactor and a temperature controller.

10 The following described preferred embodiments of the WGS catalyst can be used in each one of the first, second, and third general embodiments or in specific, related embodiments (*e.g.*, fuel cell reactors, fuel processors and hydrocarbon steam reformers.)

In a preferred embodiment, the Pt-free water gas shift catalyst comprises Ru, its oxides or mixtures thereof; Co, its oxides or mixtures thereof; and at least one of Zr, Ti, 15 Eu, their oxides and mixtures thereof.

In another preferred embodiment, the water gas shift catalyst, with an essential absence of Pt, comprises Ru, its oxides or mixtures thereof; Co, its oxides or mixtures thereof; and at least one of Cr, Mo, Fe, La, Ce, their oxides and mixtures thereof.

In another preferred embodiment, the water gas shift catalyst, with an essential 20 absence of Pt, comprises Ru, its oxides or mixtures thereof; Co, its oxides or mixtures thereof; and Mo, its oxides or mixtures thereof

In yet another preferred embodiment, the water gas shift catalyst, essential free of Pt, comprises Ru, its oxides or mixtures thereof; Co, its oxides or mixtures thereof; and at least one of Li, Na, K, Rb, Cs, Zr, their oxides and mixtures thereof. Particularly preferred 25 embodiments include Ru, Co, Na, their oxides and mixtures thereof; Ru, Co, K, their oxides and mixtures thereof; and Ru, Co, Rb, their oxides and mixtures thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are included to provide a further 30 understanding of the invention and are incorporated in and constitute a part of this

specification, illustrate preferred embodiments of the invention and together with the detailed description serve to explain the principles of the invention. In the drawings:

Figs. 1A through 1F illustrate the process of producing a library test wafer.

Figs. 2A and 2B illustrate the process of producing a library test wafer.

5 Figs. 3A through 3G illustrate the process of producing a library test wafer and
3H through 3J illustrate SpotFire plots of the CO conversion versus CO₂
production for the wafer under WGS conditions at various temperatures.

Figs. 4A through 4C illustrate the process of producing a library test wafer and
4D through 4H illustrate SpotFire plots of the CO conversion versus CO₂
10 production for the wafer under WGS conditions at various temperatures.

Figs. 5A through 5F illustrate the process of producing a library test wafer and
5G through 5I illustrate SpotFire plots of the CO conversion versus CO₂
production for the wafer under WGS conditions at various temperatures. Fig. 6
illustrates plots of CO concentration versus temperature for scaled-up catalyst samples
15 under WGS conditions.

Fig. 7 illustrates plots of CO concentration versus temperature for scaled-up
catalyst samples under WGS conditions.

Fig. 8 illustrates plots of CO concentration versus temperature for scaled-up
catalyst samples under WGS conditions.

20 Figs. 9A through 9F illustrate the compositional make-up of various exemplary
library test wafers. The legend for Figs. 9 A through C applies only to Figs. 9 A through
C. The legend for Figs. 9 D through F applies only to Figs. 9 D through F.

Fig. 10A illustrates a representative plot of CO conversion versus CO₂ production
for a prototypical library test wafer at various temperatures,

25 10B illustrates the effect of catalyst selectivity and activity versus the WGS mass
balance, and

10C illustrates the effect of temperature on catalyst performance under WGS
conditions.

Figs. 11A-11D illustrate plots of CO concentration versus temperature for scaled-
30 up catalyst samples under WGS conditions.

DETAILED DESCRIPTION OF THE INVENTION

The invention relates to a method for producing a hydrogen-rich gas, such as a hydrogen-rich syngas. According to the method a CO-containing gas, such as a syngas, contacts a water gas shift catalyst in the presence of water, preferably a stoichiometric excess of water and preferably at a reaction temperature of less than about 450 °C, to produce a hydrogen-rich gas, such as a hydrogen-rich syngas. The reaction pressure is preferably not more than about 10 bar. The invention also relates to a water gas shift catalyst itself and to apparatus such as water gas shift reactors and fuel processing apparatus comprising such WGS catalysts.

A water gas shift catalyst with an essential absence of Pt according to the invention comprises:

- (a) Ru, its oxides or mixtures thereof;
- (b) Co, Mo, their oxides or mixtures thereof; and
- (c) at least one of Li, Na, K, Rb, Cs, Ti, Zr, Cr, Fe, La, Ce, Eu, their oxides and mixtures thereof. The WGS catalyst may be supported on a carrier, such as any one member or a combination of alumina, zirconia, titania, ceria, magnesia, lanthania, niobia, zeolite, perovskite, silica clay, yttria and iron oxide.

The WGS catalysts of the invention comprise combinations of at least three metals or metalloids, selected from Ru, Co, Mo, and group c) as indicated above, in each and every possible permutation and combination, except as specifically and expressly excluded.

Discussion regarding the particular function of various components of catalysts and catalyst systems is provided herein solely to explain the advantage of the invention, and is not limiting as to the scope of the invention or the intended use, function, or mechanism of the various components and/or compositions disclosed and claimed. As such, any discussion of component and/or compositional function is made, without being bound by theory and by current understanding, unless and except such requirements are expressly recited in the claims. Generally, for example, and without being bound by theory, ruthenium metal has activity as a WGS catalyst. Co, Mo and the group of metals comprised of Li, Na, K, Rb, Cs, Ti, Zr, Cr, Fe, La, Ce and Eu may themselves have

activity as WGS catalysts but function in combination with Ru to impart beneficial properties to the catalyst of the invention.

Catalysts of the invention can catalyze the WGS reaction at varying temperatures, avoid or attenuate unwanted side reactions such as methanation reactions, as well as generate a hydrogen-rich gas, such as a hydrogen-rich syngas. The composition of the platinum-free WGS catalysts of the invention and their use in WGS reactions are discussed below.

1. Definitions

Water gas shift (WGS) reaction: Reaction which produces hydrogen and carbon dioxide from water and carbon monoxide, and vice versa:



Generally, and unless explicitly stated to the contrary, each of the WGS catalysts of the invention can be advantageously applied both in connection with the forward reaction as shown above (*i.e.*, for the production of H_2), or alternatively, in connection with the reverse reaction as shown above (*i.e.*, for the production of CO). As such, the various catalysts disclosed herein can be used to specifically control the ratio of H_2 to CO in a gas stream.

Methanation reaction: Reaction which produces methane and water from a carbon source, such as carbon monoxide or carbon dioxide, and hydrogen:



"Syngas" (also called synthesis gas): Gaseous mixture comprising hydrogen (H_2) and carbon monoxide (CO) which may also contain other gas components such as carbon dioxide (CO_2), water (H_2O), methane (CH_4) and nitrogen (N_2).

LTS: Refers to "low temperature shift" reaction conditions where the reaction temperature is less than about 250°C , preferably ranging from about 150°C to about 250°C .

MTS: Refers to “medium temperature shift” reaction conditions where the reaction temperature ranges from about 250 °C to about 350 °C.

HTS: Refers to “high temperature shift” reaction conditions where the reaction temperature is more than about 350 °C and up to about 450 °C.

5 **Hydrocarbon:** Compound containing hydrogen, carbon, and, optionally, oxygen.

The Periodic Table of the Elements is based on the present IUPAC convention, thus, for example, Group 9 comprises Co, Rh and Ir. (See <http://www.iupac.org> dated May 30, 2002).

As discussed herein, the catalyst composition nomenclature uses a dash (*i.e.*, “-”) to separate catalyst component groups where a catalyst may contain one or more of the catalyst components listed for each component group, brackets (*i.e.*, “{ }”) are used to enclose the members of a catalyst component group, “{two of}” is used if two or more members of a catalyst component group are required to be present in a catalyst composition, “blank” is used within the “{ }” to indicate the possible choice that no additional element is added, and a slash (*i.e.*, “/”) is used to separate supported catalyst components from their support material, if any. Additionally, the elements within a catalyst composition formulation include all possible oxidation states, including oxides, or salts, or mixtures thereof.

Using this shorthand nomenclature in this specification, for example, “Pt - {Rh, Ni}-{Na, K, Fe, Os}/ ZrO₂” would represent catalyst compositions containing Pt, one or more of Rh and Ni, and one or more of Na, K, Fe, and Os supported on ZrO₂; all of the catalyst elements may be in any possible oxidation state, unless explicitly indicated otherwise. “Pt-Rh-Ni-{two of Na, K, Fe, Os}” would represent a supported or unsupported catalyst composition containing Pt, Rh, and Ni, and two or more of Na, K, Fe, and Os. “Rh -{Cu,Ag,Au}-{Na, K, blank}/ TiO₂” would represent catalyst compositions containing Rh, one or more of Cu, Ag and Au, and, optionally, and one of Na or K supported on TiO₂.

The description of a catalyst composition formulation as having an essential absence of an element, or being “element-free” or “substantially element free” does allow for the presence of an insignificant, non-functional amount of the specified element to be present, for example, as a non-functional impurity in a catalyst composition formulation.

However, such a description excludes formulations where the specific element has been intentionally or purposefully added to the formulation to achieve a certain measurable benefit. Typically, with respect to noble metals such as Pt for example, amounts less than about 0.01 weight percentage would not usually impart a material functional benefit with respect to catalyst performance, and therefore such amounts would generally be considered as an insignificant amount, or not more than a mere impurity. In some embodiments, however, amounts up to less than about 0.04 weight percent may be included without a material functional benefit to catalyst performance. In other embodiments, amounts less than about 0.005 weight percent would be considered an insignificant amount, and therefore a non-functional impurity.

2. WGS Catalyst

A platinum-free water gas shift catalyst of the invention comprises:

- (a) Ru, its oxides or mixtures thereof;
- (b) Co, Mo, their oxides or mixtures thereof; and
- (c) at least one of Li, Na, K, Rb, Cs, Ti, Zr, Cr, Fe, La, Ce, Eu, their oxides and mixtures thereof. The catalyst components are typically present in a mixture of the reduced or oxide forms; typically one of the forms will predominate in the mixture. The catalysts of the invention may be supported on carriers. Suitable carriers for supported catalysts are discussed below.

A WGS catalyst of the invention may be prepared by mixing the metals and/or metalloids in their elemental forms or as oxides or salts to form a catalyst precursor. This catalyst precursor mixture generally undergoes a calcination and/or reductive treatment, which may be *in situ* (within the reactor), prior to use as a WGS catalyst. Without being bound by theory, the catalytically active species are generally understood to be species which are in the reduced elemental state or in other possible higher oxidation states. The catalyst precursor species are believed to be substantially completely converted to the catalytically active species by the pre-use treatment. Nonetheless, the catalyst component species present after calcination and/or reduction may be a mixture of catalytically active species such as the reduced metal or other possible higher oxidation states and uncalcined

or unreduced species depending on the efficiency of the calcination and/or reduction conditions.

A. Catalyst Compositions

5 As discussed above, one embodiment of the invention is a platinum-free catalyst for catalyzing the water gas shift reaction (or its reverse reaction). According to the invention, a WGS catalyst may have the following composition:

- (a) Ru, its oxides or mixtures thereof;
- (b) Co, Mo, their oxides or mixtures thereof; and
- 10 (c) at least one of Li, Na, K, Rb, Cs, Ti, Zr, Cr, Fe, La, Ce, Eu, their oxides and mixtures thereof.

The amount of each component present in a given catalyst according to the present invention may vary depending on the reaction conditions under which the catalyst is intended to operate. Generally, the ruthenium component may be present in an amount
15 ranging from about 0.01 wt. % to about 10 wt. %, preferably about 0.01 wt. % to about 2 wt. %, and more preferably about 0.05 wt. % to about 0.5 wt. %.

Cobalt may be present as either a bulk catalyst or a supported catalyst composition. Bulk cobalt catalysts may have Co concentration ranging from a high of about 90 % to a low of about 30 %, preferred is about 40 % to about 70 %; generally a bulk cobalt catalyst
20 may contain about 10 wt. % binder. Bulk cobalt catalysts may also contain other components such as zirconium, magnesium, silicon or aluminum. Supported cobalt catalysts may have Co concentrations ranging from about 0.05 % up to about 25 wt. % Co, with about 0.10 % to about 15 % a preferred range for Co concentration.

The lanthanide elements and transition metals may be present, typically, in
25 amounts ranging from about 0.05 wt. % to about 20 wt. %, preferably about 0.1 wt. % to about 15 wt. %. The main group and metalloid elements may be present in amounts ranging, generally, from about 0.01 wt. % to about 15 wt. %, preferably about 0.02 wt. % to about 10 wt. %.

The above weight percentages are calculated on the total weight of the catalyst
30 component, in its final state in the catalyst composition after the final catalyst preparation step (*i.e.*, the resulting oxidation state or states) with respect to the total weight of all catalyst components plus the support material, if any. The presence of a given catalyst

component in the support material and the extent and type of its interaction with other catalyst components may effect the amount of a component needed to achieve the desired performance effect.

In a preferred embodiment, the platinum-free water gas shift catalyst of the invention comprises Ru, Co and at least one of Zr, Ti and Eu.

In another preferred embodiment, the platinum-free water gas shift catalyst comprises Ru, Co and at least one of Cr, Mo, Fe, La and Ce. In a particularly preferred embodiment, the platinum-free water gas shift catalyst comprises Ru, Co, Fe and at least one of Cr, La and Ce. In another particularly preferred embodiment, the platinum-free catalyst comprises Ru, Co and Fe. Another particularly preferred embodiment includes Ru-Co-Fe-{Na, K}.

In yet another preferred embodiment, the platinum-free water gas shift catalyst comprises Ru and Co, at least one of Li, Na, K, Rb, Cs and Zr. Particularly preferred embodiments include Ru-Co-{Na, K, Rb} and Ru-Co-Na-Li.

In another preferred embodiment, the platinum-free water gas shift catalyst comprises Ru, Co, and Mo.

The catalysts may be more advantageously applied in specific operating temperature ranges. For instance, addition of alkali metals to the Ru-Co core significantly enhances the LTS and MTS activity of the supported or unsupported catalysts. A preferred alkali metal is Na for LTS and Na or K for MTS. Ru-Co-Na catalyst compositions maintain their high LTS and MTS activity on any support. Exemplary supports include not only zirconia, titania, bulk Co and ceria but also less expensive silicas and aluminas. One preferred embodiment is Ru and/or Na, K and Rb supported on bulk Co. A particularly preferred supported catalyst composition for LTS and MTS activity is sodium hydroxide promoted Ru-Co/ZrO₂ where sodium hydroxide is a precursor that provides the source of Na.

B. Catalyst Components a) and b): Ru and Co

Ru, its oxides or mixtures thereof and Co, its oxides or mixtures thereof are required metal components in a catalyst composition of the invention. Ru and Co may be present in an independent combination of their reduced forms and their oxides.

Unmodified Ru has been shown to catalyze the WGS reaction and is more active and less selective than Pt. Co is an example of a performance additive for Ru, along with the other components of the invention. Co may be present in the WGS catalyst compositions of the invention in a bulk state.

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C. Catalyst Component c): Components other than Ru and Co

The platinum-free WGS catalysts of the invention contain at least three metals or metalloids. In addition to the Ru and Co components discussed above, the catalyst contains metals or metalloids which, when used in combination with Ru and Co, function to impart beneficial properties to the catalyst of the invention. A catalyst of the invention, then, further comprises at least one of Li, Na, K, Rb, Cs, Ti, Zr, Cr, Mo, Fe, La, Ce, Eu, their oxides and mixtures thereof.

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D. Functional Classification of Catalyst Components

Without limiting the scope of the invention, discussion of the functions of the various catalyst components is offered, along with a template for composing catalyst compositions according to the invention. The following classification of catalyst components will direct one of skill in the art in the selection of various catalyst components to formulate WGS catalyst compositions according to the present invention and depending on the reaction conditions of interest.

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Furthermore, there are several metals which may be incorporated into a water gas shift catalyst according to the invention. Hence, the various elements recited as components in any of the described embodiments may be included in any various combination and permutation to achieve a catalyst composition that is coarsely or finely tuned for a specific application (*e.g.*, including for a specific set of conditions, such as, temperature, pressure, space velocity, catalyst precursor, catalyst loading, catalyst surface area /presentation, reactant flow rates, reactant ratios, etc.). In some cases, the effect of a given component may vary with the operating temperature for the catalyst. These catalyst components may function as, for instance, activators or moderators depending upon their effect on the performance characteristics of the catalyst. For example, if greater activity is desired, an activator may be incorporated into a catalyst, or a moderator may be replaced

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by at least one activator or, alternatively, by at least one moderator one step further up the "activity ladder." An "activity ladder" ranks secondary or added catalyst components, such as activators or moderators, in order of the magnitude of their respective effect on the performance of a principal catalyst constituent. Conversely, if WGS selectivity of a catalyst needs to be increased (*e.g.*, decrease the occurrence of the competing methanation reaction), then either an activator may be removed from the catalyst or, alternatively, the current moderator may be replaced by at least one moderator one step down the "activity ladder." The function of these catalyst components may be further described as "hard" or "soft" depending on the relative effect obtained by incorporating a given component into a catalyst. The catalyst components may be metals, metalloids, or non-metals.

As an example, the undoped combination of Ru and Co results in an active but unselective WGS catalyst at higher temperatures. Doping with a moderator of at least one of Na, K and Rb dramatically enhances selectivity of the catalyst such that the LTS and MTS selectivity approaches or surpasses Pt/ZrO₂, especially at higher temperatures. Of the doping metals, Na is the most active and efficient at LTS but K and Rb are the most selective at MTS. Additional Zr doping is expected to further enhance performance.

An example of another embodiment of a WGS catalyst of the invention is Ru-Co-Fe. The Ru-Co-Fe catalyst exhibits synergistic properties and can be used as a bulk catalyst (*e.g.*, precipitated CoFe optionally doped with other metals) or supported on conventional carriers such as zirconia, titania or ceria. At LTS and MTS, Fe acts an efficient selectivity-enhancing moderator to the otherwise too active and unselective Ru and Co combination. At higher temperatures, however, Fe becomes active on its own and therefore adds to overall activity of the Ru-Co-Fe ternary. High surface areas can be achieved by supporting the Ru-Co-Fe catalyst on conventional carriers such as, for example, zirconia and/or by adding stabilizing components such as, for example, Cr, La and Ce.

According to the present invention Ru and Co are active and selective WGS-promoting metals. The Ru-Co combination may be activated by activators which include, but are not limited to, Li, Na, K, Rb, Ti, Zr and Ce. Ce may be the most active rare earth metal for activating the WGS reaction. La and Eu may also be active, particularly at lower temperatures. In general, all lanthanides, other than Ce, show comparable performance

and tend to moderate rather than activate noble metal containing catalyst systems. La is only slightly moderating when doping Ce and may therefore be used to adjust the selectivity of Ce containing catalyst systems. Fe is an example of a selective activator over a broad dynamic range.

5 E. Supports

The support or carrier may be any support or carrier used with the catalyst which allows the water gas shift reaction to proceed. The support or carrier may be a porous, adsorptive, high surface area support with a surface area of about 25 to about 500 m²/g. The porous carrier material may be relatively inert to the conditions utilized in the WGS
10 process, and may include carrier materials that have traditionally be utilized in hydrocarbon steam reforming processes, such as, (1) activated carbon, coke, or charcoal; (2) silica or silica gel, silicon carbide, clays, and silicates including those synthetically prepared and naturally occurring, for example, china clay, diatomaceous earth, fuller's earth, kaolin, etc.; (3) ceramics, porcelain, bauxite; (4) refractory inorganic oxides such as
15 alumina, titanium dioxide, zirconium oxide, magnesia, etc.; (5) crystalline and amorphous aluminosilicates such as naturally occurring or synthetically prepared mordenite and/or faujasite; and, (6) combinations of these groups.

When a WGS catalyst of the invention is a supported catalyst, the support utilized may contain one or more of the metals (or metalloids) of the catalyst. The support may
20 contain sufficient or excess amounts of the metal for the catalyst such that the catalyst may be formed by combining the other components with the support. Examples of such supports include ceria which can contribute cerium, Ce, to a catalyst or iron oxide which can contribute iron, Fe. When such supports are used, the amount of the catalyst component in the support typically may be far in excess of the amount of the catalyst
25 component needed for the catalyst. Thus the support may act as both an active catalyst component and a support material for the catalyst. Alternatively, the support may have only minor amounts of a metal making up the WGS catalyst such that the catalyst may be formed by combining all desired components on the support.

Carrier screening with Pt as the only active noble metal revealed that a water gas
30 shift catalyst may also be supported on a carrier comprising alumina, zirconia, titania, ceria, magnesia, lanthania, niobia, zeolite, perovskite, silica clay, yttria and iron oxide.

Perovskite as well as supported perovskites (*e.g.*, supported on any of the previously listed carriers) may also be utilized as a support for the inventive catalyst formulations.

Zirconia, titania and ceria may be supports for the present invention and provide high activity for the WGS reaction. Niobia, yttria and iron oxide carriers provide high selectivity but are also less active which is believed to be due to a lack of surface area. In addition to their use as carriers, iron, yttrium and magnesium oxides may be utilized as primary layers on zirconia carriers to provide both higher surface area and low moderator concentration.

In general, alumina has been found to be an active but unselective carrier for Pt only containing WGS catalysts. However, the selectivity of gamma alumina may be improved by doping with Zr, Co, or one of the rare earth elements, such as, for example, La and Ce alone or in combination. This doping may be accomplished by addition of the oxides or other salts such as nitrates, in either liquid or solid form, to the alumina. Other possible dopants to increase the selectivity include redox dopants, such as for instance, Re, Mo, Fe, and basic dopants. Preferred is an embodiment of gamma alumina combined with Zr and/or Co which exhibits both high activity and selectivity over a broad temperature range.

High surface area aluminas, such as gamma-, delta- or theta-alumina are preferred alumina carriers. Other alumina carriers, such as mixed silica alumina, sol-gel alumina, and sol-gel or coprecipitated alumina-zirconia carriers may be used. Alumina typically has a higher surface area and a higher pore volume than carriers such as zirconia and usually offers a price advantage over other more expensive carriers.

Zirconia is a preferred carrier for use with the WGS catalysts of the invention. Monoclinic zirconia is particularly preferred. When zirconia, particularly monoclinic zirconia, is used as the catalyst carrier, the resulting catalyst compositions have shown enhanced activity under LTS conditions. That is in contrast with other carriers such as gamma alumina. This carrier effect is less pronounced for catalysts containing Na in view of Na tending to cover the surface of the carrier.

Examples of a carrier supported platinum-free WGS catalyst of the invention include: Ru-Co-{Zr, Eu, Mo, Fe, Na}/ γ -Al₂O₃, particularly Ru-Co-Zr/ γ -Al₂O₃; Ru-Co-Eu/ γ -Al₂O₃; Ru-Co-Mo/ γ -Al₂O₃; Ru-Co-Fe/ γ -Al₂O₃; and Ru-Co-Na/ γ -Al₂O₃; and

Ru-Co-{Eu, Mo, Fe, Na, blank}/ZrO₂; particularly Ru-Co-Eu/ ZrO₂; Ru-Co-Mo/ ZrO₂; Ru-Co-Fe/ ZrO₂; Ru-Co-Na/ ZrO₂; Ru-Co/ ZrO₂; Ru-Co-Fe-{Na, K}/ZrO₂ and Ru-Co-Fe-{Na, K, Zr}/ γ -Al₂O₃.

5 **F. Methods of Making a WGS Catalyst**

As set forth above, a platinum-free WGS catalyst of the invention may be prepared by mixing the metals and/or metalloids in their elemental forms or as oxides or salts to form a catalyst precursor, which generally undergoes a calcination and/or reductive treatment. Without being bound by theory, the catalytically active species are generally
10 understood to be species which are in the reduced elemental state or in other possible higher oxidation states.

The WGS catalysts of the invention may be prepared by any well known catalyst synthesis processes. See, for example, U.S. Patent Nos. 6,299,995 and 6,293,979. Spray drying, precipitation, impregnation, incipient wetness, ion exchange, fluid bed coating,
15 physical or chemical vapor deposition are just examples of several methods that may be utilized to make the present WGS catalysts. Preferred approaches, include, for instance, impregnation or incipient wetness. The catalyst may be in any suitable form, such as, pellets, granular, bed, or monolith. See also the co-pending PCT Publication No. WO 2004/058396 entitled "Methods For The Preparation Of Catalysts For Hydrogen
20 Generation" to Hagemeyer et al. for further details on methods of catalyst preparation and catalyst precursors.

The WGS catalyst of the invention may be prepared on a solid support or carrier material. Preferably, the support or carrier is, or is coated with, a high surface area
25 material onto which the precursors of the catalyst are added by any of several different possible techniques, as set forth above and as known in the art. The catalyst of the invention may be employed in the form of pellets, or on a support, preferably a monolith, for instance a honeycomb monolith.

Catalyst precursor solutions are preferably composed of easily decomposable
30 forms of the catalyst component in a sufficiently high enough concentration to permit convenient preparation. Examples of easily decomposable precursor forms include the

nitrate, amine, and oxalate salts. Typically chlorine containing precursors are avoided to prevent chlorine poisoning of the catalyst. Solutions can be aqueous or non-aqueous solutions. Exemplary non-aqueous solvents can include polar solvents, aprotic solvents, alcohols, and crown ethers, for example, tetrahydrofuran and ethanol. Concentration of the precursor solutions generally may be up to the solubility limitations of the preparation technique with consideration given to such parameters as, for example, porosity of the support, number of impregnation steps, pH of the precursor solutions, and so forth. The appropriate catalyst component precursor concentration can be readily determined by one of ordinary skill in the art of catalyst preparation.

10 **Li** – The acetate, hydroxide, nitrate and formate salts are both possible catalyst precursors for lithium.

Na – Sodium acetate, alkoxides including methoxide, propoxide, and ethoxide, bicarbonate, carbonate, citrate, formate, hydroxide, nitrate, nitrite and oxalate may be used to prepare WGS catalysts of the invention.

15 **Mg** – Water soluble magnesium precursors include the nitrate, acetate, lactate and formate salts.

K – Potassium nitrate, acetate, carbonate, hydroxide and formate are possible potassium catalyst precursors. The KOAc salt is volatile with possible potassium losses when heating up to calcination temperature.

20 **Ca** – The nitrate, acetate and hydroxide salts, preferable salts highly soluble in water, may be used to prepare catalysts of the invention.

Sc – The nitrate salt, $\text{Sc}(\text{NO}_3)_3$ may be a precursor for scandium.

Ti - Titanium precursors which may be utilized in the present invention include ammonium titanyl oxalate, $(\text{NH}_4)_2\text{TiO}(\text{C}_2\text{O}_4)_2$, available from Aldrich, and titanium(IV) bis(ammonium lactato)dihydroxide, 50 wt. % solution in water, $[\text{CH}_3\text{CH}(\text{O}-)\text{CO}_2\text{NH}_4]_2\text{Ti}(\text{OH})_2$, available from Aldrich. Other titanium containing precursors include Ti oxalate prepared by dissolving a Ti(IV) alkoxide, such as Ti(IV) propoxide, $\text{Ti}(\text{OCH}_2\text{CH}_2\text{CH}_3)_4$, (Aldrich) in 1M aqueous oxalic acid at 60 °C and stirring for a couple of hours, to produce a 0.72M clear colorless solution; $\text{TiO}(\text{acac})\text{oxalate}$ prepared by dissolving Ti(IV) oxide acetylacetonate, $\text{TiO}(\text{acac})_2$, (Aldrich) in 1.5M aqueous oxalic acid at 60 °C with stirring for a couple of hours, following by cooling to

room temperature overnight to produce 1M clear yellow-brown solution; $\text{TiO}(\text{acac})_2$, may also be dissolved in dilute acetic acid (50:50 $\text{HOAc}:\text{H}_2\text{O}$) at room temperature to produce a 1M clear yellow solution of TiO-acac . Preferably, titanium dioxide in the anatase form is utilized as a catalyst precursor material.

5 **V** - Vanadium (IV) oxalate, a vanadium precursor, may be prepared from V_2O_5 , (Aldrich), which is slurried in 1.5M aqueous oxalic acid on hot plate for 1 hour until it turns dark blue due to V(V) reduction to V(IV) by oxalic acid. Ammonium metavanadate(V), $(\text{NH}_4)\text{VO}_3$, (Cerac, Alfa) may be used as a precursor by dissolving it in water, preferably hot, about 80 °C water. Various polycarboxylic organic acid vanadium
10 precursors can be prepared and used as catalyst precursors, for example, citric, maleic, malonic, and tartaric. Vanadium citrate can be prepared by reacting V_2O_5 with citric acid, and heating to about 80 °C. Ammonium vanadium(V) oxalate may be prepared by reacting $(\text{NH}_4)\text{VO}_3$ and NH_4OH in room temperature water, increasing temperature to 90 °C, stirring to dissolve all solids, cooling to room temperature and adding oxalic acid; this
15 produces a clear orange solution, which is stable for about 2 days. Ammonium vanadium(V) citrate and ammonium vanadium(V) lactate are both prepared by shaking NH_4VO_3 in, respectively, aqueous citric acid or aqueous lactic acid, at room temperature. Diammonium vanadium(V) citrate may be prepared by dissolving, for instance, 0.25M NH_4VO_3 in citric acid diammonium salt (Alfa) at room temperature. An exemplary
20 method of preparing ammonium vanadium(V) formate is to dissolve NH_4VO_3 (0.25M) in water at 95 °C, react with 98 % formic acid and NH_4OH to produce the desired ammonium vanadium(V) formate.

Cr – Both the nitrate and acetate hydroxides are possible catalyst precursors for chromium.

25 **Mn** – Manganese nitrate, manganese acetate (Aldrich) and manganese formate (Alfa) are all possible catalyst precursors for manganese.

Fe - Iron (III) nitrate, $\text{Fe}(\text{NO}_3)_3$, iron(III) ammonium oxalate, $(\text{NH}_4)_3\text{Fe}(\text{C}_2\text{O}_4)_3$, iron(III) oxalate, $\text{Fe}_2(\text{C}_2\text{O}_4)_3$, and iron(II) acetate, $\text{Fe}(\text{OAc})_2$, are all water soluble; although the iron(III)oxalate undergoes thermal decomposition at only 100 °C. Potassium
30 iron(III) oxalate, iron(III) formate and iron(III) citrate are additional iron precursors.

Co - Both cobalt nitrate and acetate are water soluble precursor solutions. The cobalt (II) formate, $\text{Co}(\text{OOCH})_2$, has low solubility in cold water of about 5g/100mL, while cobalt (II) oxalate is soluble in aqueous NH_4OH . Another possible precursor is sodium hexanitrocobaltate(III), $\text{Na}_3\text{Co}(\text{NO}_2)_6$ which is water soluble, with gradual decomposition of aqueous solutions slowed by addition of small amounts of acetic acid. Hexaammine Co(III) nitrate is also soluble in hot (65 °C) water and NMe_4OH . Cobalt citrate, prepared by dissolving $\text{Co}(\text{OH})_2$ in aqueous citric acid at 80 °C for 1 to 2 hours, is another suitable cobalt precursor.

Ni - Nickel nitrate, $\text{Ni}(\text{NO}_3)_2$, and nickel formate are both possible nickel precursors. The nickel formate may be prepared by dissolving $\text{Ni}(\text{HCO}_2)_2$ in water and adding formic acid, or by dissolving in dilute formic acid, to produce clear greenish solutions. Nickel acetate, $\text{Ni}(\text{OAc})_2$, is also a nickel precursor. Nickel chloride, NiCl_2 , may also be used when precipitating nickel salts such as nickel hydroxide or nickel carbonate. In contrast to catalyst compositions containing noble metals, base metal catalysts, such as bulk Ni, are not poisoned by chloride.

Cu - Copper precursors include nitrate, $\text{Cu}(\text{NO}_3)_2$, acetate, $\text{Cu}(\text{OAc})_2$, and formate, $\text{Cu}(\text{OOCH})_2$, which are increasingly less water soluble in the order presented. Ammonium hydroxide is used to solublize oxalate, $\text{Cu}(\text{C}_2\text{O}_4)_2$, and $\text{Cu}(\text{NH}_3)_4(\text{OH})_2$ which is soluble in aqueous 5N NH_4OH . Copper citrate and copper amine carbonate may be prepared from $\text{Cu}(\text{OH})_2$.

Zn - Zinc nitrate, acetate and formate are all water soluble and possible catalyst precursors. Ammonium zinc carbonate, $(\text{NH}_4)_2\text{Zn}(\text{OH})_2\text{CO}_3$, prepared by reacting zinc hydroxide and ammonium carbonate for a week at room temperature, is another possible precursor for zinc.

Ge - Germanium oxalate may be prepared from amorphous Ge(IV) oxide, glycol-soluble GeO_2 , (Aldrich) by reaction with 1M aqueous oxalic acid at room temperature. H_2GeO_3 may be prepared by dissolving GeO_2 in water at 80 °C and adding 3 drops of NH_4OH (25 %) to produce a clear, colorless H_2GeO_3 solution. $(\text{NMe}_4)_2\text{GeO}_3$ may be prepared by dissolving 0.25M GeO_2 in 0.1M NMe_4OH . $(\text{NH}_4)_2\text{GeO}_3$ may be prepared by dissolving 0.25 M GeO_2 in 0.25M NH_4OH .

Rb – The nitrate, acetate, carbonate and hydroxide salts may be used as catalyst precursors to prepare the WGS catalyst of the invention. Preferred are water soluble salts.

Sr – The acetate is soluble in cold water to produce a clear colorless solution.

Y – Yttrium nitrate and acetate are both possible catalyst precursors.

5 **Zr** – Zirconyl nitrate and acetate, commercially available from Aldrich, and ammonium Zr carbonate and zirconia, available from MEI, are possible precursors for zirconium in either or both the support or catalyst formulation itself.

10 **Nb** - Niobium oxalate prepared by dissolving niobium (V) ethoxide in aqueous oxalic acid at 60 °C for 12 hours is a possible catalyst precursor. Another preparative route to the oxalate is dissolving niobic acid or niobic oxide (Nb_2O_5) in oxalic acid at 65 °C. Ammonium Nb oxalate is also a possible catalyst precursor for niobium. Dissolving niobic oxide (0.10M Nb) in NMe_4OH (0.25M) and stirring overnight at 65 °C will produce $(\text{NMe}_4)_2\text{NbO}_6$.

15 **Mo** - Molybdenum containing precursor solutions may be derived from ammonium molybdate $(\text{NH}_4)_2\text{MoO}_4$ (Aldrich) dissolved in room temperature water; Mo oxalate prepared by dissolving MoO_3 (Aldrich) in 1.5M aqueous oxalic acid at 60 °C overnight; and ammonium Mo oxalate prepared from $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (Strem) dissolved in 1M aqueous oxalic acid at room temperature. $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (Strem) may also be dissolved in water at room temperature to produce a stable solution of ammonium paramolybdate tetrahydrate. Molybdic acid, H_2MoO_4 , (Alfa Aesar or Aldrich) may each be dissolved in room temperature water to produce 1M Mo containing solutions.

20 **Ru** - Ru nitrosyl nitrate, $\text{Ru}(\text{NO})(\text{NO}_3)_3$ (Aldrich), potassium ruthenium oxide, $\text{K}_2\text{RuO}_4\cdot\text{H}_2\text{O}$, potassium perruthenate, KRuO_4 , ruthenium nitrosyl acetate, $\text{Ru}(\text{NO})(\text{OAc})_3$, and tetrabutylammonium perruthenate, NBu_4RuO_4 , are all possible ruthenium metal catalyst precursors. $\text{NMe}_4\text{Ru}(\text{NO})(\text{OH})_4$ solution can be prepared by dissolving $\text{Ru}(\text{NO})(\text{OH})_3$ (0.1 M) (H.C. Starck) in NMe_4OH (0.12M) at 80 °C produces a clear dark red-brown 0.1M Ru solution useful as a catalyst precursor solution.

Rh - A suitable rhodium catalyst precursor is Rh nitrate (Aldrich or Strem).

30 **Pd** - Catalyst compositions containing Pd can be prepared by using precursors like Pd nitrate, typically stabilized by dilute HNO_3 , and available as a 10 wt. % solution from

Aldrich, or $\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2$ available as a 5 wt. % Pd commercial solution, stabilized by dilute NH_4OH . $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$ and $\text{Pd}(\text{NH}_3)_4(\text{OH})_2$ are also available commercially.

Ag – Silver nitrate, silver nitrite, silver diammine nitrite, and silver acetate are possible silver catalyst precursors.

5 **Cd** – Cadmium nitrate is water soluble and a suitable catalyst precursor.

In – Indium formate and indium nitrate are preferred precursors for indium.

Sn - Tin oxalate produced by reacting the acetate with oxalic acid may be used as a catalyst precursor. Tin tartrate, $\text{SnC}_4\text{H}_4\text{O}_6$, in NMe_4OH at about 0.25M Sn concentration, and tin acetate, also dissolved in NMe_4OH at about 0.25M Sn concentration, may be used
10 as catalyst precursors.

Sb - Ammonium antimony oxalate produced by reacting the acetate with oxalic acid and ammonia is a suitable antimony precursor. Antimony oxalate, $\text{Sb}_2(\text{C}_2\text{O}_4)_3$, available from Pfaltz & Bauer, is a water soluble precursor. Potassium antimony oxide, KSbO_3 , and antimony citrate, prepared by stirring antimony(II) acetate in 1M citric acid at
15 room temperature, are both possible catalyst precursors.

Te - Telluric acid, $\text{Te}(\text{OH})_6$, may be used as a precursor for tellurium.

Cs - Cs salts including the nitrate, acetate, carbonate, and hydroxide are soluble in water and possible catalyst precursors.

Ba - Barium acetate and barium nitrate are both suitable precursors for barium
20 catalyst components.

La - Lanthanum precursors include nitrate, $\text{La}(\text{NO}_3)_3$, acetate, $\text{La}(\text{OAc})_3$, and perchlorate, $\text{La}(\text{ClO}_4)_3$, all of which may be prepared as aqueous solutions.

Ce - Ce(III) and Ce(IV) solutions may be prepared from Ce(III) nitrate hexahydrate, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, (Aldrich) and ammonium cerium(IV) nitrate, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, (Aldrich), respectively, by dissolution in room temperature water. Nitric
25 acid, 5 vol. %, may be added to the Ce(III) salt to increase solubility and stability. $\text{Ce}(\text{OAc})_3$ (Alfa) or $\text{Ce}(\text{NO}_3)_4$ (Alfa) may also be utilized as a catalyst precursor.

Pr, Nd, Sm and Eu – The nitrate, $\text{Ln}(\text{NO}_3)_3$, or acetate, $\text{Ln}(\text{O}_2\text{CCH}_3)_3$, are possible catalyst precursors for these lanthanides.

Hf – Hafnium chloride and nitrate are both possible precursors. Preparing the hafnium nitrate by dissolving $\text{Hf}(\text{acac})_4$ in dilute HNO_3 at low heat provides a clear stable solution of hafnium nitrate.

Ta – Tantalum oxalate solution, $\text{Ta}_2\text{O}(\text{C}_2\text{O}_4)_4$, available from H. C. Starck, or prepared by dissolving $\text{Ta}(\text{OEt})_5$ in aqueous oxalic acid at 60 °C for 12 hours, is a possible catalyst precursor.

W – Ammonium metatungstate hydrate, $(\text{NH}_4)_6\text{W}_{12}\text{O}_{39}$, is water soluble and a possible tungsten catalyst precursor. H_2WO_4 is reacted with NH_4OH and NMe_4OH , respectively, to prepare $(\text{NH}_4)_2\text{WO}_4$ and $(\text{NMe}_4)_2\text{WO}_4$ which are both possible precursors.

Re – Rhenium oxide in H_2O_2 , perrhenic acid, (HReO_4) , NaReO_4 and NH_4ReO_4 are suitable rhenium precursors.

Ir – Hexachloroiridate acid, H_2IrCl_6 , potassium hexacyanoiridate and potassium hexanitroiridate are all possible catalyst precursors for iridium.

Pt – Platinum containing catalyst compositions may be prepared by using any one of a number of precursor solutions, such as, $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ (Aldrich, Alfa, Heraeus, or Strem), $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ in nitric acid, $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$ (Alfa), $\text{K}_2\text{Pt}(\text{NO}_2)_4$, $\text{Pt}(\text{NO}_3)_2$, PtCl_4 and H_2PtCl_6 (chloroplatinic acid). $\text{Pt}(\text{NH}_3)_4(\text{HCO}_3)_2$, $\text{Pt}(\text{NH}_3)_4(\text{HPO}_4)$, $(\text{NMe}_4)_2\text{Pt}(\text{OH})_6$, $\text{H}_2\text{Pt}(\text{OH})_6$, $\text{K}_2\text{Pt}(\text{OH})_6$, $\text{Na}_2\text{Pt}(\text{OH})_6$ and $\text{K}_2\text{Pt}(\text{CN})_6$ are also possible choices along with Pt oxalate salts, such as $\text{K}_2\text{Pt}(\text{C}_2\text{O}_4)_2$. The Pt oxalate salts may be prepared from $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$ which is reacted with 1M oxalic acid solution to produce a clear, colorless solution of the desired Pt oxalate salts.

Au – Auric acid, HAuCl_4 , in dilute HCl at about 5 % Au may be a gold precursor. Gold nitrate in 0.1M concentration may be prepared by dissolving $\text{HAu}(\text{NO}_3)_4$ (Alfa) in concentrated nitric acid, followed by stirring at room temperature for 1 week in the dark, then diluting 1:1 with water to produce a yellow solution. It should be noted that further dilution may result in Au precipitation. More concentrated, 0.25M, for example, gold nitrate may be prepared by starting with $\text{Au}(\text{OH})_3$ (Alfa). $\text{NaAu}(\text{OH})_4$, $\text{KAu}(\text{OH})_4$, and $\text{NMe}_4\text{Au}(\text{OH})_4$ may each be prepared from $\text{Au}(\text{OH})_3$ dissolved in bases NaOH , KOH , or NMe_4OH , respectively, in base concentrations ranging from, for instance, 0.25M or higher.

3. Producing a Hydrogen-rich Gas, such as, a Hydrogen-rich Syngas

The invention also relates to a method for producing a hydrogen-rich gas, such as, a hydrogen-rich syngas. An additional embodiment of the invention may be directed to a method of producing a CO-depleted gas, such as a CO-depleted syngas.

5 A CO-containing gas, such as a syngas, contacts with a water gas shift catalyst in the presence of water according to the method of the invention. The reaction preferably may occur at a temperature of less than 450°C to produce a hydrogen-rich gas, such as a hydrogen-rich syngas.

A method of the invention may be utilized over a broad range of reaction
10 conditions. Preferably, the method is conducted at a pressure of no more than about 75 bar, preferably at a pressure of no more than about 50 bar to produce a hydrogen-rich syngas. Even more preferred is to have the reaction occur at a pressure of no more than about 25 bar, or even no more than about 15 bar, or not more than about 10 bar. Especially preferred is to have the reaction occur at, or about atmospheric pressure.
15 Depending on the formulation of the catalyst according to the present invention, the present method may be conducted at reactant gas temperatures ranging from less than about 250 °C to up to about 450 °C. Preferably, the reaction occurs at a temperature selected from one or more temperature subranges of LTS, MTS and/or HTS as described above. Space velocities may range from about 1 hr⁻¹ up to about 1,000,000 hr⁻¹. Feed
20 ratios, temperature, pressure and the desired product ratio are factors that would normally be considered by one of skill in the art to determine a desired optimum space velocity for a particular catalyst formulation.

4. Fuel Processor Apparatus

25 The invention further relates to a fuel processing system for generation of a hydrogen-rich gas from a hydrocarbon or substituted hydrocarbon fuel. Such a fuel processing system would comprise, for example, a fuel reformer, a water gas shift reactor and a temperature controller.

The fuel reformer would convert a fuel reactant stream comprising a hydrocarbon
30 or a substituted hydrocarbon fuel to a reformed product stream comprising carbon monoxide and water. The fuel reformer may typically have an inlet for receiving the

reactant stream, a reaction chamber for converting the reactant stream to the product stream, and an outlet for discharging the product stream.

The fuel processor system would also comprise a water gas shift reactor for effecting a water gas shift reaction at a temperature of less than about 450 °C. This water gas shift reactor may comprise an inlet for receiving a water gas shift feed stream comprising carbon monoxide and water from the product stream of the fuel reformer, a reaction chamber having a water gas shift catalyst as described herein located therein, and an outlet for discharging the resulting hydrogen-rich gas. The water gas shift catalyst would preferable be effective for generating hydrogen and carbon dioxide from the water gas shift feed stream.

The temperature controller may be adapted to maintain the temperature of the reaction chamber of the water gas shift reactor at a temperature of less than about 450 °C .

15 5. Industrial Applications

Syngas is used as a reactant feed in number of industrial applications, including for example, methanol synthesis, ammonia synthesis, oxoaldehyde synthesis from olefins (typically in combination with a subsequent hydrogenation to form the corresponding oxoalcohol), hydrogenations and carbonylations. Each of these various industrial applications preferably includes a certain ratio of H₂ to CO in the syngas reactant stream. For methanol synthesis the ratio of H₂:CO is preferably about 2:1. For oxosynthesis of oxoaldehydes from olefins, the ratio of H₂:CO is preferably about 1:1. For ammonia synthesis, the ratio of H₂ to N₂ (e.g., supplied from air) is preferably about 3:1. For hydrogenations, syngas feed streams that have higher ratios of H₂:CO are preferred (e.g., feed streams that are H₂ enriched, and that are preferably substantially H₂ pure feed streams). Carbonylation reactions are preferably effected using feed streams that have lower ratios of H₂:CO (e.g., feed streams that are CO enriched, and that are preferably substantially CO pure feed streams).

30 The WGS catalysts of the present invention, and the methods disclosed herein that employ such WGS catalysts, can be applied industrially to adjust or control the relative ratio H₂:CO in a feed stream for a synthesis reaction, such as methanol synthesis,

ammonia synthesis, oxoaldehyde synthesis, hydrogenation reactions and carbonylation reactions. In one embodiment, for example, a syngas product stream comprising CO and H₂ can be produced from a hydrocarbon by a reforming reaction in a reformer (*e.g.*, by steam reforming of a hydrocarbon such as methanol or naphtha). The syngas product stream can then be fed (directly or indirectly after further downstream processing) as the feed stream to a WGS reactor, preferably having a temperature controller adapted to maintain the temperature of the WGS reactor at a temperature of about 450 °C or less during the WGS reaction (or at lower temperatures or temperature ranges as described herein in connection with the catalysts of the present invention). The WGS catalyst(s) employed in the WGS reactor are preferably selected from one or more of the catalysts and/or methods of the invention. The feed stream to the WGS reactor is contacted with the WGS catalyst(s) under reaction conditions effective for controlling the ratio of H₂:CO in the product stream from the WGS reactor (*i.e.*, the "shifted product stream") to the desired ratio for the downstream reaction of interest (*e.g.*, methanol synthesis), including to ratios described above in connection with the various reactions of industrial significance. As a non-limiting example, a syngas product stream from a methane steam reformer will typically have a H₂:CO ratio of about 6:1. The WGS catalyst(s) of the present invention can be employed in a WGS reaction (in the forward direction as shown above) to further enhance the amount of H₂ relative to CO, for example to more than about 10:1, for a downstream hydrogenation reaction. As another example, the ratio of H₂:CO in such a syngas product stream can be reduced by using a WGS catalyst(s) of the present invention in a WGS reaction (in the reverse direction as shown above) to achieve or approach the desired 2:1 ratio for methanol synthesis. Other examples will be known to a person of skill in the art in view of the teachings of the present invention.

A person of skill in the art will understand and appreciate that with respect to each of the preferred catalyst embodiments as described in the preceding paragraphs, the particular components of each embodiment can be present in their elemental state, or in one or more oxide states, or mixtures thereof.

Although the foregoing description is directed to the preferred embodiments of the invention, it is noted that other variations and modifications will be apparent to those

skilled in the art, and which may be made without departing from the spirit or scope of the invention.

EXAMPLES

5 General

Small quantity catalyst composition samples are generally prepared by automated liquid dispensing robots (Cavro Scientific Instruments) on flat quartz test wafers.

Generally, supported catalysts are prepared by providing a catalyst support (*e.g.* alumina, silica, titania, *etc.*) to the wafer substrate, typically as a slurry composition using
10 a liquid-handling robot to individual regions or locations on the substrate or by wash-coating a surface of the substrate using techniques known to those of skill in the art, and drying to form dried solid support material on the substrate. Discrete regions of the support-containing substrate are then impregnated with specified compositions intended to operate as catalysts or catalyst precursors, with the compositions comprising metals (*e.g.*
15 various combinations of transition metal salts). In some circumstances the compositions are delivered to the region as a mixture of different metal-containing components and in some circumstances (additionally or alternatively) repeated or repetitive impregnation steps are performed using different metal-containing precursors. The compositions are dried to form supported catalyst precursors. The supported catalyst precursors are treated
20 by calcining and/or reducing to form active supported catalytic materials at discrete regions on the wafer substrate.

Bulk catalysts (*e.g.* noble-metal-free Co-containing catalysts) may also be prepared on the substrate. Such multi-component bulk catalysts are purchased from a commercial source and/or are prepared by precipitation or co-precipitation protocols, and then
25 optionally treated – including mechanical pretreatment (grinding, sieving, pressing). The bulk catalysts are placed on the substrate, typically by slurry dispensing and drying, and then optionally further doped with additional metal-containing components (*e.g.* metal salt precursors) by impregnation and/or incipient wetness techniques to form bulk catalyst precursors, with such techniques being generally known to those of skill in the art. The
30 bulk catalyst precursors are treated by calcining and/or reducing to form active bulk catalytic materials at discrete regions on the wafer substrate.

The catalytic materials (*e.g.*, supported or bulk) on the substrate are tested for activity and selectivity for the WGS reaction using a scanning mass spectrometer ("SMS") comprising a scanning / sniffing probe and a mass spectrometer. More details on the scanning mass spectrometer instrument and screening procedure are set forth in U.S. Patent No. 6,248,540, in European Patent No. EP 101994 and in European Patent Application No. EP 1186892 and corresponding U.S. Patent No. 6,864,091.

Generally, the reaction conditions (*e.g.* contact time and/or space velocities, temperature, pressure, *etc.*) associated with the scanning mass spectrometer catalyst screening reactor are controlled such that partial conversions (*i.e.*, non-equilibrium conversions, *e.g.*, ranging from about 10 % to about 40 % conversion) are obtained in the scanning mass spectrometer, for discrimination and ranking of catalyst activities for the various catalytic materials being screened. Additionally, the reaction conditions and catalyst loadings are established such that the results scale appropriately with the reaction conditions and catalyst loadings of larger scale laboratory research reactors for WGS reactions. A limited set of tie-point experiments are performed to demonstrate the scalability of results determined using the scanning mass spectrometer to those using larger scale laboratory research reactors for WGS reactions. See, for example, Example 12 of U.S. Patent No. 7,160,533 entitled "Platinum-Ruthenium Containing Catalyst Formulations for Hydrogen Generation".

Preparative and Testing Procedures

The catalysts and compositions of the present invention were identified using high-throughput experimental technology, with the catalysts being prepared and tested in library format, as described generally above, and in more detail below. Specifically, such techniques were used for identifying catalyst compositions that were active and selective as WGS catalysts. As used in these examples, a "catalyst library" refers to an associated collection of candidate WGS catalysts arrayed on a wafer substrate, and having at least two, and typically three or more common metal components (including metals in the fully

reduced state, or in a partially or fully oxidized state, such as metal salts), but differing from each other with respect to relative stoichiometry of the common metal components.

Depending on the library design and the scope of the investigation with respect to a particular library, multiple (*i.e.*, two or more) libraries were typically formed on each wafer substrate. A first group of test wafers each comprised about 100 different catalyst compositions formed on a three-inch wafer substrate, typically with most catalysts being formed using at least three different metals. A second group of test wafers each comprised about 225 different catalyst compositions on a four-inch wafer substrate, again typically with most catalysts being formed using at least three different metals. Each test wafer itself typically comprised multiple libraries. Each library typically comprised binary, ternary or higher-order compositions – that is, for example, as ternary compositions that comprised at least three components (*e.g.*, A, B, C) combined in various relative ratios to form catalytic materials having a molar stoichiometry covering a range of interest (*e.g.*, typically ranging from about 20 % to about 80 % or more (*e.g.* to about 100 % in some cases) of each component). For supported catalysts, in addition to varying component stoichiometry for the ternary compositions, relative total metal loadings were also investigated.

Typical libraries formed on the first group of (three-inch) test wafers included, for example, “five-point libraries” (*e.g.*, twenty libraries, each having five different associated catalyst compositions), or “ten-point” libraries (*e.g.*, ten libraries, each having ten different associated catalyst compositions), or “fifteen-point libraries” (*e.g.*, six libraries, each having fifteen different associated catalyst compositions) or “twenty-point libraries” (*e.g.*, five libraries, each having twenty different associated catalyst compositions). Typical libraries formed on the second group of (four-inch) test wafers included, for example, “nine-point libraries” (*e.g.*, twenty-five libraries, each having nine different associated catalyst compositions), or “twenty-five point” libraries (*e.g.*, nine libraries, each having twenty-five different associated catalyst compositions). Larger compositional investigations, including “fifty-point libraries” (*e.g.*, two or more libraries on a test wafer, each having fifty associated catalyst compositions), were also investigated. Typically, the stoichiometric increments of candidate catalyst library members ranged from about 1.5 % (*e.g.* for a “fifty-five point ternary”) to about 15 % (*e.g.*, for a “five-point” ternary). See,

generally, for example, WO 00/17413 for a more detailed discussion of library design and array organization. Figs. 9A to 9F of the instant application show library designs for libraries prepared on a common test wafer, as graphically represented using Library Studio[®] (Symyx Technologies, Inc., Santa Clara, CA), where the libraries vary with
 5 respect to both stoichiometry and catalyst loading. Libraries of catalytic materials that vary with respect to relative stoichiometry and/or relative catalyst loading can also be represented in a compositional table, such as is shown in the several examples of this application.

Referring to Fig. 9A, for example, the test wafer includes nine libraries, where
 10 each of the nine libraries comprise nine different ternary compositions of the same three-component system. In the nomenclature of the following examples, such a test wafer is said to include nine, nine-point-ternary ("9PT") libraries. The library depicted in the upper right hand corner of this test wafer includes catalyst compositions comprising components A, B and X₁ in 9 different stoichiometries. As another example, with
 15 reference to Fig. 9B, a partial test wafer is depicted that includes a fifteen-point-ternary ("15PT") library having catalyst compositions of Pt, Pd and Cu in fifteen various stoichiometries. Generally, the composition of each catalyst included within a library is graphically represented by an association between the relative amount (*e.g.*, moles or weight) of individual components of the composition and the relative area shown as
 20 corresponding to that component. Hence, referring again to the fifteen different catalyst compositions depicted on the partial test wafer represented in Fig. 9B, it can be seen that each composition includes Pt (dark grey), Pd (light grey) and Cu (black), with the relative amount of Pt increasing from column 1 to column 5 (but being the same as compared between rows within a given column), with the relative amount of Pd decreasing from row
 25 1 to row 5 (but being the same as compared between columns within a given row), and with the relative amount of Cu decreasing from a maximum value at row 5, column 1 to a minimum at, for example, row 1, column 1. Fig. 9C shows a test wafer that includes a fifty-point-ternary ("50PT") library having catalyst compositions of Pt, Pd and Cu in fifty various stoichiometries. This test library could also include another fifty-point ternary
 30 library (not shown), for example with three different components of interest.

Figs. 9D through 9F are graphical representations of two fifty-point ternary libraries (“*bis* 50PT libraries”) at various stages of preparation – including a Pt-Au-Ag/CeO₂ library (shown as the upper right ternary library of Fig. 9E) and a Pt-Au-Ce/ZrO₂ library (shown as the lower left ternary library of Fig. 9E). Note that the Pt-Au-Ag/CeO₂ library also includes binary-impregnated compositions – Pt-Au/CeO₂ binary catalysts (row 2) and Pt-Ag/CeO₂ (column 10). Likewise, the Pt-Au-Ce/ZrO₂ library includes binary-impregnated compositions – Pt-Ce/ZrO₂ (row 11) and Au-Ce/ZrO₂ (column 1). Briefly, the *bis* 50PT libraries were prepared by depositing CeO₂ and ZrO₂ supports onto respective portions of the test wafer as represented graphically in Fig. 9D. The supports were deposited onto the test wafer as a slurry in a liquid media using a liquid handling robot, and the test wafer was subsequently dried to form dried supports. Thereafter, salts of Pt, Au and Ag were impregnated onto the regions of the test wafer containing the CeO₂ supports in the various relative stoichiometries as represented in Fig. 9E (upper-right-hand library). Likewise, salts of Pt, Au and Ce were impregnated onto the regions of the test wafer containing the ZrO₂ supports in the various relative stoichiometries as represented in Fig. 9E (lower-left-hand library). Fig. 9F is a graphical representation of the composite library design, including the relative amount of catalyst support.

Specific compositions of tested catalytic materials of the invention are detailed in the following examples for selected libraries.

Performance benchmarks and reference experiments (*e.g.*, blanks) were also provided on each quartz catalyst test wafer as a basis for comparing the catalyst compositions of the libraries on the test wafer. The benchmark catalytic material formulations included a Pt/zirconia catalyst standard with about 3 % Pt catalyst loading (by weight, relative to total weight of catalyst and support). The Pt/zirconia standard was typically synthesized by impregnating 3 μ L of, for example, 1.0 % or 2.5 % by weight Pt stock solution onto zirconia supports on the wafer prior to calcination and reduction pretreatment.

Typically wafers were calcined in air at a temperature ranging from 300 °C to 500 °C and/or reduced under a continuous flow of 5 % hydrogen at a temperature ranging from about 200 °C to about 500 °C (*e.g.*, 450 °C). Specific treatment protocols are described below with respect to each of the libraries of the examples.

For testing using the scanning mass spectrometer, the catalyst wafers were mounted on a wafer holder which provided movement in an XY plane. The sniffing/scanning probe of the scanning mass spectrometer moved in the Z direction (a direction normal to the XY plane of movement for the wafer holder), and approached in close proximity to the wafer to surround each independent catalyst element, deliver the feed gas and transmit the product gas stream from the catalyst surface to the quadrupole mass spectrometer. Each element was heated locally from the backside using a CO₂ laser, allowing for an accessible temperature range of about 200 °C to about 600 °C. The mass spectrometer monitored seven masses for hydrogen, methane, water, carbon monoxide, argon, carbon dioxide and krypton: 2, 16, 18, 28, 40, 44 and 84, respectively.

Catalyst compositions were tested at various reaction temperatures, typically including for example at about 300 °C, 350 °C and/or 400 °C and, additionally, usually for more active formulations, at 250 °C. Particularly for LTS formulations, testing of catalytic activity at reaction temperatures starting as low as 200 °C may occur. The feed gas typically consisted of 51.6 % H₂, 7.4 % Kr, 7.4 % CO, 7.4 % CO₂ and 26.2 % H₂O. The H₂, CO, CO₂ and Kr internal standards are premixed in a single gas cylinder and then combined with the water feed. Treated water (18.1 mega-ohms-cm at 27.5 °C) produced by a Barnstead Nano Pure Ultra Water system was used, without degassing.

20 Data Processing and Analysis

Data analysis was based on mass balance plots where CO conversion was plotted versus CO₂ production. The mass spectrometer signals were uncalibrated for CO and CO₂ but were based on Kr-normalized mass spectrometer signals. The software package Spotfire™ (sold by Spotfire, Inc. of Somerville, Massachusetts) was used for data visualization.

A representative plot of CO conversion versus CO₂ production for a WGS reaction is shown in Fig. 10A involving, for discussion purposes, two ternary catalyst systems – a Pt-Au-Ag/CeO₂ catalyst library and a Pt-Au-Ce/ZrO₂ catalyst library – as described above in connection with Figs. 9D through 9F. The catalyst compositions of these libraries were screened at four temperatures: 250 °C, 300 °C, 350 °C and 400 °C. With reference to the schematic diagram shown in Fig. 10B, active and highly selective WGS catalysts (e.g.,

Line I of Fig. 10B) will approach a line defined by the mass balance for the water-gas-shift reaction (the "WGS diagonal") with minimal deviation, even at relatively high conversions (*i.e.*, at CO conversions approaching the thermodynamic equilibrium conversion (point "TE" on Fig. 10B)). Highly active catalysts may begin to deviate from the WGS diagonal due to cross-over to the competing methanation reaction (point "M" on Fig. 10C). Catalyst compositions that exhibit such deviation may still, however, be useful WGS catalysts depending on the conversion level at which such deviation occurs. For example, catalysts that first deviate from the WGS diagonal at higher conversion levels (*e.g.*, Line II of Fig. 10B) can be employed as effective WGS catalysts by reducing the overall conversion (*e.g.*, by lowering catalyst loading or by increasing space velocity) to the operational point near the WGS diagonal. In contrast, catalysts that deviate from the WGS diagonal at low conversion levels (*e.g.*, Line III of Fig. 10B) will be relatively less effective as WGS catalysts, since they are unselective for the WGS reaction even at low conversions. Temperature affects the thermodynamic maximum CO conversion, and can affect the point of deviation from the mass-balance WGS diagonal as well as the overall shape of the deviating trajectory, since lower temperatures will generally reduce catalytic activity. For some compositions, lower temperatures will result in a more selective catalyst, demonstrated by a WGS trajectory that more closely approximates the WGS mass-balance diagonal. (See Fig. 10C). Referring again to Fig. 10A, it can be seen that the Pt-Au-Ag/CeO₂ and the Pt-Au-Ce/ZrO₂ catalyst compositions are active and selective WGS catalysts at each of the screened temperatures, and particularly at lower temperatures.

Generally, the compositions on a given wafer substrate were tested together in a common experimental run using the scanning mass spectrometer and the results were considered together. In this application, candidate catalyst compositions of a particular library on the substrate (*e.g.*, ternary or higher-order catalysts comprising three or more metal components) were considered as promising candidates for an active and selective commercial catalyst for the WGS reaction based on a comparison to the Pt/ZrO₂ standard composition included on that wafer. Specifically, libraries of catalytic materials were deemed to be particularly preferred WGS catalysts if the results demonstrated that a meaningful number of catalyst compositions in that library compared favorably to the

Pt/ZrO₂ standard composition included on the wafer substrate with respect to catalytic performance. In this context, a meaningful number of compositions was generally considered to be at least three of the tested compositions of a given library. Also in this context, favorable comparison means that the compositions had catalytic performance that

5 was as good as or better than the standard on that wafer, considering factors such as conversion, selectivity and catalyst loading. All catalyst compositions of a given library were in many cases positively identified as active and selective WGS catalysts even in situations where only some of the library members compared favorably to the Pt/ZrO₂ standard, and other compositions within that library compared less than favorably to the

10 Pt/ZrO₂ standard. In such situations, the basis for also including members of the library that compared somewhat less favorably to the standard is that these members in fact positively catalyzed the WGS reaction (*i.e.* were effective as catalysts for this reaction). Additionally, it is noted that such compositions may be synthesized and/or tested under more optimally tuned conditions (*e.g.*, synthesis conditions, treatment conditions and/or

15 testing conditions (*e.g.*, temperature)) than occurred during actual testing in the library format, and significantly, that the optimal conditions for the particular catalytic materials being tested may differ from the optimal conditions for the Pt/ZrO₂ standard – such that the actual test conditions may have been closer to the optimal conditions for the standard than for some of the particular members. Therefore, it was specifically contemplated that

20 optimization of synthesis, treatment and/or screening conditions, within the generally defined ranges of the invention as set forth herein, would result in even more active and selective WGS catalysts than what was demonstrated in the experiments supporting this invention. Hence, in view of the foregoing discussion, the entire range of compositions defined by each of the claimed compositions (*e.g.*, each three-component catalytic

25 material, or each four-component catalytic material) was demonstrated as being effective for catalyzing the WGS reaction. Further optimization is considered, with various specific advantages associated with various specific catalyst compositions, depending on the desired or required commercial application of interest. Such optimization can be achieved, for example, using techniques and instruments such as those described in U.S.

30 Patent No. 6,149,882 or those described in WO 01/66245 and its corresponding U.S. Publication No. US 2002/2048536 entitled “Parallel Flow Process Optimization Reactor”

and U.S. Publication No. US 2002/0045265 entitled "Parallel Flow Reactor Having Variable Feed Composition".

Additionally, based on the results of screening of initial libraries, selective
 5 additional "focus" libraries were selectively prepared and tested to confirm the results of
 the initial library screening, and to further identify better performing compositions, in
 some cases under the same and/or different conditions. The test wafers for the focus
 libraries typically comprised about 225 different candidate catalyst compositions formed
 on a four-inch wafer substrate, with one or more libraries (e.g. associated ternary
 10 compositions A, B, C) formed on each test wafer. Again, the metal-containing
 components of a given library were typically combined in various relative ratios to form
 catalysts having stoichiometry ranging from about 0 % to about 100 % of each component,
 and for example, having stoichiometric increments of about 10 % or less, typically about 2
 % or less (e.g., for a "fifty-six point ternary"). Focus libraries are more generally
 15 discussed, for example, in WO 00/17413. Such focus libraries were evaluated according
 to the protocols described above for the initial libraries.

The raw residual gas analyzer (rga) signal values generated by the mass
 spectrometer for the individual gases are uncalibrated and therefore different gases may
 not be directly compared. Methane data (mass 16) was also collected as a control. The
 20 signals are typically standardized by using the raw rga signal for krypton (mass 84) to
 remove the effect of gas flow rate variations. Thus, for each library element, the
 standardized signal is determined as, for example, $s_{H_2O} = \text{raw } H_2O / \text{raw Kr}$; $s_{CO} = \text{raw } CO / \text{raw Kr}$; $s_{CO_2} = \text{raw } CO_2 / \text{raw Kr}$ and so forth.

Blank or inlet concentrations are determined from the average of the standardized
 25 signals for all blank library elements (i.e. library elements for which the composition
 contains at most only support). For example, $b_{avg} H_2O = \text{average } s_{H_2O}$ for all blank
 elements in the library; $b_{avg} CO = \text{average } s_{CO}$ for all blank elements in the library; and so
 forth.

Conversion percentages are calculated using the blank averages to estimate the
 30 input level (e.g., $b_{avg} CO$) and the standardized signal (e.g., s_{CO}) as the output for each

library element of interest. Thus, for each library element, $\text{CO}_{\text{conversion}} = 100 \times (\text{b}_{\text{avg}} \text{CO} - \text{sCO})/\text{b}_{\text{avg}} \text{CO}$ and $\text{H}_2\text{O}_{\text{conversion}} = 100 \times (\text{b}_{\text{avg}} \text{H}_2\text{O} - \text{sH}_2\text{O})/\text{b}_{\text{avg}} \text{H}_2\text{O}$.

The carbon monoxide (CO) to carbon dioxide (CO₂) selectivity is estimated by dividing the amount of CO₂ produced ($\text{sCO}_2 - \text{b}_{\text{avg}} \text{CO}_2$) by the amount of CO consumed ($\text{b}_{\text{avg}} \text{CO} - \text{sCO}$). The CO₂ and CO signals are not directly comparable because the rga signals are uncalibrated. However, an empirical conversion constant (0.6 CO₂ units = 1 CO unit) has been derived, based on the behavior of highly selective standard catalyst compositions. The selectivity of the highly selective standard catalyst compositions approach 100 % selectivity at low conversion rates. Therefore, for each library element, estimated CO to CO₂ selectivity = $100 \times 0.6 \times (\text{sCO}_2 - \text{b}_{\text{avg}} \text{CO}_2)/(\text{b}_{\text{avg}} \text{CO} - \text{sCO})$. Low CO consumption rates can produce highly variable results, and thus the reproducibility of CO₂ selectivity is maintained by artificially limiting the CO₂ selectivity to a range of 0 % to 140 %.

15

The following examples are representative of the screening of libraries that lead to identification of the particularly claimed inventions herein.

Example 1:

20 A 4" quartz wafer was pre-coated with 14 columns of Engelhard Co-164 (bulk Co commercial catalyst) and ZrO₂ (Norton XZ16052) as reference carrier by slurry dispensing as a master batch in volumes of 3 μL (both 1.5 g/ 4 mL, EG/H₂O/MeO 32.5:30:37.5) to a 15x15 square on the wafer. After the dispensing step the wafer was oven-dried at 70 °C for 14 minutes.

25 Six internal standards were synthesized by Cavo spotting 3 μL of Pt(NH₃)₂(NO₂)₂ (stabilized, 2.5 % Pt) stock solution into the corresponding first row/last column positions. The Co-bulk carrier pre-coated wafer was impregnated with a ruthenium(III) nitrosyl nitrate (diluted in dilute nitric acid and containing 1.5 % Ru) gradient from top to bottom by Cavo dispensing from the respective stock solution vial to a microtiter plate and
30 diluting with distilled water followed by a one-to-one transfer of the microtiter plate pattern to the wafer. The Ru solution was dispensed in 2.5 μL dispense volume per well

resulting in a 14 x 15 point rectangle on the wafer (14 replicas of the 15 point Ru gradients).

Subsequently the ZrO_2 pre-coated carrier column no.15 was impregnated with a 15 point single column $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ (unstabilized, 1 % Pt) gradient from bottom to top by
 5 Cavo dispensing from the corresponding stock Pt solution vial to a microtiter plate and diluting with distilled water followed by a one-to-one transfer to the wafer by dispensing 2.5 μL dispense volume per well.

The wafer was slowly dried overnight at room temperature. The Co-bulk carrier coated columns nos. 2–14 were coated with binary metal-gradients from bottom to top:
 10 C2: LiOH , C3: KOH , C4: NaOH , C5: RbOH (C2-C5: 1 molar), C6: $\text{Fe}(\text{NO}_3)_3$, C7: H_2MoO_4 , C8: $\text{Ce}(\text{III})(\text{NO}_3)_3$, C9: $\text{La}(\text{NO}_3)_3$ (C6-C9: 0.25 molar), C10: H_2IrCl_6 (1 % Ir), C11: $\text{Cu}(\text{NO}_3)_2$ (0.1 molar), C12: $\text{Mn}(\text{NO}_3)_2$ (0.25 molar), C13: $\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2$ (1 % Pd), C14: $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ (unstabilized, 1 % Pt), by Cavo dispensing 2.5 μL per well from the respective stock solution vials as above resulting in a 13 x 15 point rectangle on the wafer.
 15 The wafer was slowly dried at room temperature for 3 hours and then reduced in a flow of 5 % H_2/N_2 at 450 °C for 2 hours. Commercial catalyst was slurried into five positions of the first row and last column as external standard (3 μL catalyst slurry). See Figs. 1A through 1F. The wafer was screened by SMS for WGS activity with a $\text{H}_2/\text{CO}/\text{CO}_2/\text{H}_2\text{O}$ mixed feed at 200 °C, 230 °C and 260 °C.

20 This set of experiments demonstrated active and selective bulk cobalt supported WGS catalyst formulations.

Example 2:

A 4" quartz wafer was precoated with ZrO_2 carrier by repeated slurry dispensing of
 25 zirconia powder (Norton XZ16052/MEI FZO923/01 70:30 mix) onto the wafer (1g zirconia powder in 4 mL EG/ H_2O 50:50 mixture, 2 zirconia layers = $2 \times 3 \mu\text{L} = 6\mu\text{L}$ slurry dispensed in total). The zirconia carrier-precoated wafer was dried and then impregnated with gradients of the metals (Co, Ni, Cu, Fe and Ru). Advantageously, all metal precursor solutions (metal nitrates and Ru nitrosyl nitrate) are compatible and a single impregnation
 30 step suffices to deposit all the metals. The gradients were premixed in a microtiter plate by dilution of metal nitrate stock solutions with water. The diluted solutions are then

transferred from the microtiter plate to the wafer by Cavo dispensing (3 μ L dispense volume per well). The wafer was dried, calcined in air at 500 °C for 1 hour and then reduced in 5 % H₂/Ar at 380 °C for 3 hours. See Figs. 2A and 2B.

The reduced wafer was then screened by SMS for WGS activity with a
5 H₂/CO/CO₂/H₂O mixed feed at 250 °C, 300 °C, 350 °C and 400 °C.

This set of experiments demonstrated active and selective WGS catalyst formulations for Ru and Co containing formulations supported on zirconia.

Example 3:

10 A 4" quartz wafer was precoated with zirconia carrier by repeated slurry dispensing zirconia powder (Norton XZ16052) onto the wafer. The slurry was composed of 1.5g zirconia powder in 4 mL of a MEO/EG/H₂O 40:30:30 mixture. A total of 3 μ L of slurry was deposited on each spot.

The zirconia carrier precoated wafer was impregnated with separate concentration
15 gradients of Co, Fe, Sm, Ge, Sn and Ti by Cavo dispensing from metal stock solution vials to a microtiter plate (five, four, one, two, one, two columns, respectively of each metal in 7-point ("7P") and 8-point ("8P") concentration gradients) followed by transferring replicas of the four 7P and 8P columns onto the wafer (2.5 μ L dispense volume per well). The wafer was dried at 70 °C for 10 minutes.

20 The wafer was then impregnated with Fe, Zr, Ti, Mo, Eu, Sn, Sb and V concentration gradients by Cavo dispensing 2.5 μ L per well in 7-point and 8-point gradients. The metal columns were arranged in the following order beginning on the left: Fe, Zr, Ti, Mo, Eu, Zr, Ti, Mo, Eu, Eu, Sn, Sb, Sb, V and Mo. For all of the above impregnations, Co, Fe, Sm and Eu were provided as their nitrates, Ge, Sn and V as their
25 oxalates, Ti as the ammonium titanyl oxalate, Sb as the ammonium antimony oxalate, Zr as zirconyl nitrate and Mo as molybdic acid. The wafer was dried at 70 °C for 10 minutes.

The top seven rows of the wafer were uniformly coated with 2.5 μ L per well of a RuNO(NO₃)₃ stock solution (0.5 % Ru), and the bottom eight rows were uniformly coated
30 in air at 400 °C for 2 hours followed by reduction with 5 % H₂/N₂ at 300 °C for 2 hours.

Nine internal standards were synthesized by spotting 2.5 μL $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ solution (2.5 % Pt) into the corresponding first row/last column positions. See Figs. 3A through 3G.

The reduced library was then screened in SMS for WGS activity with a $\text{H}_2/\text{CO}/\text{CO}_2/\text{H}_2\text{O}$ mixed feed at 300 °C and 350 °C. The CO conversion versus CO_2 production results at 300 °C and 350 °C are presented in Figs. 3H and 3I. More detailed test results, such as, CO conversion, CO_2 production and CH_4 production at 300 °C and 350 °C for each of the 225 individual catalyst wells on the test wafer are presented in Table 1.

This set of experiments demonstrated active and selective WGS catalyst formulations of various Ru-Co-{Fe, Zr, Ti, Mo, Eu,}/ ZrO_2 formulations on the wafer.

Example 4:

A 3" quartz wafer was coated with niobia, ceria and magnesia carriers by slurry-dispensing aqueous carrier slurries onto the wafer (4 μL slurry/well, 1 g of carrier powder slurried in 2 mL H_2O for niobia and ceria; 500 mg of carrier powder slurried in 2 mL H_2O for magnesia). Niobia carriers were produced by Norton, product numbers 2001250214, 2000250356, 2000250355, 2000250354 and 2000250351. Cerias came from Norton (product numbers 2001080053, 2001080052 and 2001080051) and Aldrich (product number 21,157-50). Magnesia was obtained from Aldrich (product number 24,338-8).

The carrier precoated wafer was then loaded with the same Pt gradient for each carrier in a single impregnation step by liquid dispensing 3 μL $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ solution (5 % Pt) from microtiter plate to wafer. The wafer was dried and then reduced in 5 % H_2/Ar at 450 °C for 2 hours. See Figs. 4A through 4C.

The reduced library was then screened in SMS for WGS activity with a $\text{H}_2/\text{CO}/\text{CO}_2/\text{H}_2\text{O}$ mixed feed at 250 °C, 300 °C, 350 °C, and 400 °C. Results at 250 °C, 300 °C, 350 °C, and 400 °C are presented in Figs. 4D through 4H.

This set of experiments demonstrated active and selective WGS catalyst formulations of various Pt on one of Nb oxide, Ce oxide or Mg oxide formulations on the wafer. Various Norton niobia carriers were found to be very active and selective over a broad temperature range. Norton ceria 2001080051 was found to be very selective at

higher temperatures. Magnesia was less active than either of niobia or ceria but did exhibit highly selective WGS performance.

Example 5:

5 A 4" quartz wafer was coated with fourteen different catalyst carriers by slurry-dispensing the carrier slurries onto the wafer. Each wafer column was coated with a different carrier, except for columns 14 and 15 which were both coated with gamma-alumina, described below:

1) Ceria, 99.5 % purity; 9 to 15 nm particle size; BET (m^2/g): 55-95; Alfa 43136;
10 dispensed onto the wafer from a slurry of 0.75 g powder slurried in 4 mL ethylene glycol ("EG")/ H_2O /MEO 40:30:30 mixture.

2) Ceria, produced by the low temperature calcination of precipitated Ce hydroxide; dispensed onto the wafer from a slurry of 1.5 g powder slurried in 4 mL EG/ H_2O /MEO 40:30:30 mixture.

15 3) Zirconia; 99.8 % purity; BET (m^2/g): greater than 90; Norton XZ16052; dispensed onto the wafer from a slurry of 1.5 g powder slurried in 4 mL EG/ H_2O /MEO 40:30:30 mixture.

4) Zirconia; 99.8 % purity; BET (m^2/g): 269; Norton XZ16154; dispensed onto the wafer from a slurry of 1.5 g powder slurried in 4 mL EG/ H_2O /MEO 40:30:30 mixture.

20 5) Titania; BET (m^2/g): 45; Degussa Aerolyst 7708; dispensed onto the wafer from a slurry of 1.0 g powder slurried in 4 mL EG/ H_2O /MEO 40:30:30 mixture.

6) Titania; 99 % purity; BET (m^2/g): 37; Norton XT25384; dispensed onto the wafer from a slurry of 1.0 g powder slurried in 4 mL EG/ H_2O /MEO 40:30:30 mixture.

7) Niobia; 97 % purity; BET (m^2/g): 27; Norton 2000250355; dispensed onto the
25 wafer from a slurry of 1.0 g powder slurried in 4 mL EG/ H_2O /MEO 40:30:30 mixture.

8) Lanthania; 99.999 % purity; Gemre-5N from Gemch Co., Ltd. (Shanghai, China); dispensed onto the wafer from a slurry of 1.5 g powder slurried in 4 mL EG/ H_2O /MEO 40:30:30 mixture.

9) Mixed Fe-Ce-O; coprecipitated Fe and Ce oxalate; calcined at 360 °C;
30 dispensed onto the wafer from a slurry of 1.0 g powder slurried in 4 mL EG/ H_2O /MEO 40:30:30 mixture.

10) Mixed La-Ce-O; coprecipitated La and Ce oxalate; calcined at 760 °C; dispensed onto the wafer from a slurry of 1.0 g powder slurried in 4 mL EG/H₂O/MEO 40:30:30 mixture.

11) Mixed Sb₃O₄-SnO₂ carrier from Alfa; 99.5 % purity; BET (m²/g): 30-80; 5 Sb₃O₄:SnO₂ ratio is 10:90 by weight; dispensed onto the wafer from a slurry of 1.0 g powder slurried in 4 mL EG/H₂O/MEO 40:30:30 mixture.

12) Mixed Fe-Cr-Al-O; commercially available high temperature water gas shift catalyst; dispensed onto the wafer from a slurry of 1.0 g powder slurried in 4 mL EG/H₂O/MEO 40:30:30 mixture.

10 13) Fe₂O₃/FeOOH; BET (m²/g): 14; 50:50 physical mixture of commercial powders (Bayferrox 720N: Bayoxide E3920 from Bayer); dispensed onto the wafer from a slurry of 1.0 g powder slurried in 4 mL EG/H₂O/MEO 40:30:30 mixture.

14 and 15) Gamma-Al₂O₃; BET (m²/g): 150; Condea Catalox Sba150; dispensed 15 onto the wafer from a slurry of 1.0 g powder slurried in 4 mL EG/H₂O/MEO 40:30:30 mixture.

In all cases, except for carrier 1, the slurries were applied in 3 µl/well; carrier 1 was deposited as two aliquots of 3 µL per well. The wafer was then dried at 70 °C for 10 minutes.

Columns 14 and 15 were coated with 2.5 µl/well of zirconyl nitrate (0.25M) and 20 lanthanum nitrate (0.25M), respectively, then dried for 10 minutes at 70 °C. The first 13 columns of the carrier coated wafer were then loaded with a 15 point Pt gradient by liquid dispensing of 3 µL Pt(NH₃)₂(NO₂)₂ solution (1 % Pt) from microtiter plate to wafer. The wafer was dried at 70 °C for 10 minutes. Columns 14 and 15 were then loaded with a 15 point Pt gradient by liquid dispensing of 3 µL Pt(NH₃)₂(NO₂)₂ solution (1 % Pt) from 25 microtiter plate to wafer. The wafer was dried at 70 °C for 10 minutes, calcined in air at 350 °C for 2 hours, then reduced in 5 % H₂/Ar at 450 °C for 2 hours. Six internal standards were synthesized by spotting 3 µL Pt(NH₃)₂(NO₂)₂ solution (1.0 % Pt) into the corresponding first row/last column positions. See Figs. 5A through 5F.

The reduced library was then screened in SMS for WGS activity with a 30 H₂/CO/CO₂/H₂O mixed feed at 250 °C and 300 °C. The CO conversion versus CO₂ production results at 250 °C and 300 °C are presented in Figs. 5G, 5H and 5I. More

detailed test results, such as, CO conversion, CO₂ production and CH₄ production at 250 °C and 300 °C for each of the 225 individual catalyst wells on the test wafer are presented in Table 2.

This set of experiments demonstrated active and selective WGS catalyst formulations of various Pt on various of the oxide carrier formulations on the wafer.

Example 6:

Scale-up catalyst samples were prepared by using incipient wetness impregnation of 0.75 grams of ZrO₂ support (Norton, 80-120 mesh) which had been weighed into a 10-dram vial. Aqueous metal precursor salt solutions were then added in the order: Ru, Fe, one of Co or Mo, then Na. The precursor salt solutions were ruthenium (III) nitrosyl nitrate (1.5 % Ru (w/v)), iron (III) nitrate (1.0M), cobalt (II) nitrate (1.0M), molybdic acid (1.0M), and sodium hydroxide (3.0N). All starting reagents were nominally research grade and purchased from Aldrich, Strem, or Alfa. Following each metal addition, the catalysts were dried at 80° C overnight and then calcined in air as follows:

After Ru addition	--	450 °C for 3 hours
After Fe addition	--	450 °C for 3 hours
After Co or Mo addition	--	450 °C for 3 hours for Co, 350 °C for 3 hours for Mo.

Following Na addition, the catalysts were calcined at 300 °C for 3 hours, and then the catalysts were reduced *in-situ* at 300 °C for 3 hours in a 10% H₂/N₂ feed.

Catalyst Testing Conditions

Catalysts were tested in a fixed bed reactor. Approximately 0.15 g of catalyst was weighed and mixed with an equivalent mass of SiC. The mixture was loaded into a reactor and heated to reaction temperature. Reaction gases were delivered via mass flow controllers (Brooks) with water introduced with a metering pump (Quizix). The composition of the reaction mixture was as follows: H₂ 50%, CO 10%, CO₂ 10%, and H₂O 30%. The reactant mixture was passed through a pre-heater before contacting the catalyst bed. Following reaction, the product gases were analyzed using a micro gas

chromatograph (Varian Instruments, or Shimadzu). Compositional data on the performance diagram (Fig. 6) is on a dry basis with water removed.

Testing Results

- 5 Fig. 6 shows the CO composition in the product stream following the scale-up testing at a gas hour space velocity of $50,000 \text{ h}^{-1}$.

Table 3: Catalyst Compositions (mass ratio)

Row	Col	Support	Ru	Co	Fe	Na	Mo
A	1	0.95	0.01	0.005	0.01	0.025	0
A	2	0.94	0.01	0.005	0.02	0.025	0
A	3	0.93	0.01	0.005	0.03	0.025	0
A	4	0.94	0.02	0.005	0.01	0.025	0
A	5	0.93	0.02	0.005	0.02	0.025	0
A	6	0.92	0.02	0.005	0.03	0.025	0
B	1	0.945	0.01	0.01	0.01	0.025	0
B	2	0.935	0.01	0.01	0.02	0.025	0
B	3	0.925	0.01	0.01	0.03	0.025	0
B	4	0.935	0.02	0.01	0.01	0.025	0
B	5	0.925	0.02	0.01	0.02	0.025	0
B	6	0.915	0.02	0.01	0.03	0.025	0
C	1	0.95	0.01	0	0.01	0.025	0.005
C	2	0.94	0.01	0	0.02	0.025	0.005
C	3	0.93	0.01	0	0.03	0.025	0.005
C	4	0.94	0.02	0	0.01	0.025	0.005
C	5	0.93	0.02	0	0.02	0.025	0.005
C	6	0.92	0.02	0	0.03	0.025	0.005
D	1	0.945	0.01	0	0.01	0.025	0.01
D	2	0.935	0.01	0	0.02	0.025	0.01
D	3	0.925	0.01	0	0.03	0.025	0.01

Row	Col	Support	Ru	Co	Fe	Na	Mo
D	4	0.935	0.02	0	0.01	0.025	0.01
D	5	0.925	0.02	0	0.02	0.025	0.01
D	6	0.915	0.02	0	0.03	0.025	0.01

Example 7:

Scale-up catalyst samples were prepared by using incipient wetness impregnation of 0.75 grams of ZrO_2 support (Norton, 80-120 mesh) which had been weighed into a 10-dram vial. Aqueous metal precursor salt solutions were then added in the order: Ru, one of Co or Mo, then one of Na or K. The precursor salt solutions were ruthenium (III) nitrosyl nitrate (1.5 % Ru w/v), cobalt (II) nitrate (1.0M), molybdic acid (1.0M), potassium hydroxide (13.92 % K w/v), and sodium hydroxide (3.0N). All starting reagents were nominally research grade and purchased from Aldrich, Strem, or Alfa.

Following each metal addition, the catalysts were dried at 80° C overnight and then calcined in air as follows:

After Ru addition -- 450 °C for 3 hours

After Co or Mo addition -- 450 °C for 3 hours for Co, 350 °C for 3 hours for Mo

After Na or K addition -- 300 °C for 3 hours

Following Na addition, the catalysts were calcined at 300 °C for 3 hours, and then the catalysts were reduced *in-situ* at 300 °C for 3 hours in a 10% H_2/N_2 feed.

Catalyst Testing Conditions

Catalysts were tested in a fixed bed reactor. Approximately 0.15 g of catalyst was weighed and mixed with an equivalent mass of SiC. The mixture was loaded into a reactor and heated to reaction temperature. Reaction gases were delivered via mass flow controllers (Brooks) with water introduced with a metering pump (Quizix). The composition of the reaction mixture was as follows: H_2 50%, CO 10%, CO_2 10%, and H_2O 30%. The reactant mixture was passed through a pre-heater before contacting the catalyst bed. Following reaction, the product gases were analyzed using a micro gas chromatograph (Varian Instruments, or Shimadzu). Compositional data on the performance diagram (Fig. 7) is on a dry basis with water removed.

Testing Results

Fig. 7 shows the CO composition in the product stream following the scale-up testing at a gas hour space velocity of $50,000 \text{ h}^{-1}$.

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Table 4: Catalyst Compositions (mass ratio)

Row	Col	Support	Ru	Co	Na	K	Mo
A	1	0.95	0.02	0.005	0.025	0	0
A	2	0.925	0.02	0.005	0.05	0	0
A	3	0.93	0.04	0.005	0.025	0	0
A	4	0.95	0.02	0.005	0	0.025	0
A	5	0.925	0.02	0.005	0	0.05	0
A	6	0.93	0.04	0.005	0	0.025	0
B	1	0.945	0.02	0.01	0.025	0	0
B	2	0.92	0.02	0.01	0.05	0	0
B	3	0.925	0.04	0.01	0.025	0	0
B	4	0.945	0.02	0.01	0	0.025	0
B	5	0.92	0.02	0.01	0	0.05	0
B	6	0.925	0.04	0.01	0	0.025	0
C	1	0.95	0.02	0	0.025	0	0.005
C	2	0.925	0.02	0	0.05	0	0.005
C	3	0.93	0.04	0	0.025	0	0.005
C	4	0.95	0.02	0	0	0.025	0.005
C	5	0.925	0.02	0	0	0.05	0.005
C	6	0.93	0.04	0	0	0.025	0.005
D	1	0.945	0.02	0	0.025	0	0.01
D	2	0.92	0.02	0	0.05	0	0.01
D	3	0.925	0.04	0	0.025	0	0.01
D	4	0.945	0.02	0	0	0.025	0.01
D	5	0.92	0.02	0	0	0.05	0.01

D	6	0.925	0.04	0	0	0.025	0.01
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Example 8:

- Scale-up catalyst samples were prepared by using incipient wetness impregnation of 0.75 grams of ZrO_2 support (Norton, 80-120 mesh) which had been weighed into a 10-dram vial. Aqueous metal precursor salt solutions were then added in the order: Ru, Fe, Mo and K. The precursor salt solutions were ruthenium (III) nitrosyl nitrate (1.5 % Ru (w/v)), iron (III) nitrate (1.0M), molybdic acid (1.0M), and potassium hydroxide (13.92 % K (w/v)). All starting reagents were nominally research grade and purchased from Aldrich, Strem, or Alfa.
- Following each metal addition, the catalysts were dried at 80° C overnight and then calcined in air as follows:
- After Ru addition -- 450 °C for 3 hours
- After Fe addition -- 450 °C for 3 hours
- After Mo addition -- 350 °C for 3 hours.
- Following K addition, the catalysts were calcined at 300 °C for 3 hours, and then the catalysts were reduced *in-situ* at 300 °C for 3 hours in a 10% H_2/N_2 feed.

Catalyst Testing Conditions

- Catalysts were tested in a fixed bed reactor. Approximately 0.15 g of catalyst was weighed and mixed with an equivalent mass of SiC. The mixture was loaded into a reactor and heated to reaction temperature. Reaction gases were delivered via mass flow controllers (Brooks) with water introduced with a metering pump (Quizix). The composition of the reaction mixture was as follows: H_2 50%, CO 10%, CO_2 10%, and H_2O 30%. The reactant mixture was passed through a pre-heater before contacting the catalyst bed. Following reaction, the product gases were analyzed using a micro gas chromatograph (Varian Instruments, or Shimadzu). Compositional data on the performance diagram is on a dry basis with water removed.

Testing Results

Fig. 8 shows the CO composition in the product stream following the scale-up testing at a gas hour space velocity of 50,000 h⁻¹.

Table 5: Catalyst Compositions (mass ratio)

Row	Col	Zr Oxide	Ru	Water	Fe	Mo	K
A	1	90.5	1	0	1.5	2	5
A	2	89	1	0	3	2	5
A	3	89.5	2	0	1.5	2	5
A	4	88	2	0	3	2	5
A	5	88.5	3	0	1.5	2	5
A	6	87	3	0	3	2	5
B	1	88.5	1	0	1.5	4	5
B	2	87	1	0	3	4	5
B	3	87.5	2	0	1.5	4	5
B	4	86	2	0	3	4	5
B	5	86.5	3	0	1.5	4	5
B	6	85	3	0	3	4	5
C	1	86.5	1	0	1.5	6	5
C	2	85	1	0	3	6	5
C	3	85.5	2	0	1.5	6	5
C	4	84	2	0	3	6	5
C	5	84.5	3	0	1.5	6	5
C	6	83	3	0	3	6	5
D	1	84.5	1	0	1.5	8	5
D	2	83	1	0	3	8	5
D	3	83.5	2	0	1.5	8	5
D	4	82	2	0	3	8	5
D	5	82.5	3	0	1.5	8	5
D	6	81	3	0	3	8	5

Example 9:

Scale-up catalyst samples were prepared by using incipient wetness impregnation of 0.75 grams of ZrO_2 support (Norton, 80-120 mesh) which had been weighed into a 10-dram vial. Aqueous metal precursor salt solutions were then added in the order: Ru, Fe, Co, K. The precursor salt solutions were ruthenium (III) nitrosyl nitrate (1.5 % Ru (w/v)), iron (III) nitrate (1.0M), cobalt (II) nitrate (1.0M), and potassium hydroxide (13.92 % K (w/v)). All starting reagents were nominally research grade purchased from Aldrich, Strem, or Alfa. Following each metal addition, the catalysts were dried at 80° C overnight and then calcined in air as follows:

- 10 After Ru addition -- 450 °C for 3 hours
 After Fe or Co addition -- 450 °C for 3 hours

Following K addition, the catalysts were calcined at 300 °C for 3 hours, and then the catalysts were reduced *in-situ* at 300 °C for 3 hours in a 10% H_2/N_2 feed.

15 **Catalyst Testing Conditions**

Catalysts were tested in a fixed bed reactor. Approximately 0.15 g of catalyst was weighed and mixed with an equivalent mass of SiC. The mixture was loaded into a reactor and heated to reaction temperature. Reaction gases were delivered via mass flow controllers (Brooks) with water introduced with a metering pump (Quizix). The composition of the reaction mixture was as follows: H_2 50%, CO 10%, CO_2 10%, and H_2O 30%. The reactant mixture was passed through a pre-heater before contacting the catalyst bed. Following reaction, the product gases were analyzed using a micro gas chromatograph (Varian Instruments, or Shimadzu). Compositional data on the performance diagrams (Figs. 11A-11D) is on a dry basis with water removed.

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Testing Results

Figs. 11A-11D show the CO composition in the product stream following the scale-up testing at a gas hour space velocity of $50,000 \text{ h}^{-1}$.

30 **Table 6: Catalyst Compositions (mass ratio)**

Row	Col	ZrO2	Ru	Water	Co	Fe	K
A	1	90.5	1	0	2	1.5	5
A	2	89	1	0	2	3	5
A	3	89.5	2	0	2	1.5	5
A	4	88	2	0	2	3	5
A	5	88.5	3	0	2	1.5	5
A	6	87	3	0	2	3	5
B	1	88.5	1	0	4	1.5	5
B	2	87	1	0	4	3	5
B	3	87.5	2	0	4	1.5	5
B	4	86	2	0	4	3	5
B	5	86.5	3	0	4	1.5	5
B	6	85	3	0	4	3	5
C	1	86.5	1	0	6	1.5	5
C	2	85	1	0	6	3	5
C	3	85.5	2	0	6	1.5	5
C	4	84	2	0	6	3	5
C	5	84.5	3	0	6	1.5	5
C	6	83	3	0	6	3	5
D	1	84.5	1	0	8	1.5	5
D	2	83	1	0	8	3	5
D	3	83.5	2	0	8	1.5	5
D	4	82	2	0	8	3	5
D	5	82.5	3	0	8	1.5	5
D	6	81	3	0	8	3	5

Table I

Fe	Si	Al	Ca	Mg	Na	K	Cl	S	P	Cr	Mn	Co	Ni	Cu	Zn	As	Sb	Te	Se	Mo	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Pb	Bi	Po	At	Rn	Ac	Th	Pa
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3	8	0.74	0.6287	-0.0325	-1.1919	-0.0042	0	0	0.375	0	0.875	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	9	58.6781	-2.952	0.6094	22.3277	0.4362	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	10	54.7072	-25.9679	0.2052	7.5179	0.8253	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	11	5.9726	-0.7412	0.1289	4.7248	0.027	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	12	3.4876	0.0838	0.1318	4.4615	0.0136	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	13	1.0476	-1.4924	0.0231	0.8115	0.01	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	14	0.3148	-0.6654	-0.0142	-0.5186	-0.0004	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	15	0.6877	0.4516	-0.0215	-0.706	-0.0053	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	16	1.0421	-0.3365	-0.0228	-0.8031	-0.0004	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	17	31.8656	4.81	0.6317	22.7821	0.3062	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	18	46.6604	-11.5483	0.4504	14.3016	0.6186	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	19	33.8092	1.1877	0.5488	26.089	0.3832	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	20	1.2781	-1.9499	-0.0827	-1.565	-0.0016	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	21	48.8802	-11.6772	0.3364	13.9897	0.6563	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	22	34.8348	0.9453	0.6246	22.7751	0.3756	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	23	10.5793	7.3969	0.3882	28.9264	0.0465	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	24	1.3085	0.3801	-0.0317	-1.1612	-0.0048	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	25	42.2767	-3.7441	0.6055	22.1853	0.6907	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	26	33.9575	-19.4847	0.3258	8.2743	0.8018	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	27	53.0398	3.7753	0.1589	6.7749	0.0146	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	28	4.6881	3.909	0.1452	5.3289	0.0187	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	29	1.2289	-0.657	0.0944	1.7959	0.0024	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	30	-0.7192	-1.6325	-0.0389	-0.803	-0.0001	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	31	3.7864	1.3939	-0.0897	-0.3555	-0.0046	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	32	28.4391	9.7211	0.9002	32.9827	0.2801	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	33	48.6212	-6.0883	0.5584	20.4618	0.5161	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	34	44.6688	-18.8634	0.4511	14.5275	0.6095	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	35	37.3534	-4.2781	0.8367	22.1564	0.4259	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	36	1.5689	-1.9895	-0.0317	-0.0898	0.0002	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	37	26.1298	14.1131	0.4311	13.4311	0.6837	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	38	26.6419	0.0223	0.4334	23.3728	0.2194	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	39	8.4684	3.7946	0.281	18.2848	0.044	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	40	0.9779	-0.8846	-0.0178	-0.446	-0.0031	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	41	35.2543	4.8889	0.707	25.9658	0.3905	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	42	54.6799	-31.1561	0.2862	7.585	0.8254	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	43	5.2864	1.4731	0.1243	4.5549	0.0252	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	44	5.3536	4.3433	0.119	4.3991	0.0158	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	45	3.3075	1.1382	0.6441	1.6145	0.0066	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	46	0.3153	-1.9202	-0.0269	-0.0849	0.0033	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	47	-0.3673	-0.4322	-0.0057	-0.2048	0.0023	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	48	1.4925	1.2273	-0.0321	-1.1769	-0.0028	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	49	42.7555	-9.0717	0.5895	19.7664	0.5614	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	50	45.8288	-8.9258	0.4896	18.3052	0.6147	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	51	41.5856	-1.708	0.6264	22.9528	0.4638	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	52	8.6842	5.2728	0.2394	8.7703	0.0789	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	53	48.6176	-9.6213	0.494	18.1089	0.6381	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	54	19.4889	12.4448	0.6144	22.5119	0.083	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	55	7.7294	5.7291	0.224	8.2883	0.0237	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	56	1.568	1.0613	-0.0066	-0.2431	-0.0038	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	57	28.3066	6.7237	0.7747	28.3872	0.2406	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	58	33.6389	-21.8164	0.2283	8.3731	0.8224	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	59	8.4889	0.0813	0.1556	5.7026	0.023	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	60	1.746	4.324	0.1794	6.5737	0.0211	0	0	0.375	0	0	0	0	0	0.1225	0	0	1.3725	0	0	27.32	0	63.75	0	0	8.93	0	0
3	61	1.4512	2.879	0.0482	1.7673	0.0029	0	0																				

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2	8	4.2902	1.5276	0.1017	3.728	0.0316	0	0	0.0319	0	0.0319	0	100	0
2	9	17.5859	9.8527	0.5611	20.5685	0.0868	0	0	0.0319	0	0.0319	0	100	0
2	10	4.0056	0.7967	0.1073	3.9343	0.0337	0	0	0.0319	0	0.0319	0	100	0
2	11	0.4511	-1.4852	-0.0262	-0.9611	0.0142	0	0	0.0319	0	0.0319	0	100	0
2	12	8.7515	3.1358	0.2704	9.9096	0.0534	0	0	0.0319	0	0.0319	0	100	0
2	13	1.1667	-0.4291	0.0028	0.1022	0.0172	0	0	0.0319	0	0.0319	0	100	0
2	14	5.3788	3.039	0.1661	6.0891	0.0402	0	0	0.0319	0.625	0.6569	0	4.85	95.15
2	15	13.8175	7.9862	0.4538	16.6329	0.0753	0	0.625	0.0319	0	0.6569	95.15	4.85	0
2	16	0.5892	0.0397	-0.0171	-0.6274	-0.0021	0	0	0	0	0	0	0	0
3	1	23.0341	14.9411	0.7335	26.8867	0.1082	0	0	0.0387	0	0.0387	0	100	0
3	2	24.8268	16.0912	0.7611	27.8973	0.108	0	0	0.0387	0	0.0387	0	100	0
3	3	21.0312	12.2163	0.6617	24.2545	0.0974	0	0	0.0387	0	0.0387	0	100	0
3	4	15.3062	8.5994	0.4563	16.7247	0.0714	0	0	0.0387	0	0.0387	0	100	0
3	5	13.1818	6.4699	0.3775	13.8381	0.0651	0	0	0.0387	0	0.0387	0	100	0
3	6	14.4778	9.2713	0.4241	15.5437	0.0643	0	0	0.0387	0	0.0387	0	100	0
3	7	5.5717	3.3425	0.1029	3.772	0.0251	0	0	0.0387	0	0.0387	0	100	0
3	8	6.8228	1.6923	0.1521	5.5733	0.0283	0	0	0.0387	0	0.0387	0	100	0
3	9	18.2423	12.1678	0.5606	20.5468	0.0831	0	0	0.0387	0	0.0387	0	100	0
3	10	6.7011	5.5857	0.1612	5.907	0.033	0	0	0.0387	0	0.0387	0	100	0
3	11	1.3529	1.3312	-0.0328	-1.2024	0.0065	0	0	0.0387	0	0.0387	0	100	0
3	12	8.988	6.9454	0.2544	9.3233	0.0421	0	0	0.0387	0	0.0387	0	100	0
3	13	1.9882	1.6201	-0.0124	-0.4561	0.0102	0	0	0.0387	0	0.0387	0	100	0
3	14	6.7207	4.8802	0.1283	4.7036	0.0288	0	0	0.0387	0.625	0.6637	0	5.83	94.17
3	15	13.1254	7.8413	0.4144	15.1912	0.0623	0	0.625	0.0387	0	0.6637	94.17	5.83	0
3	16	1.6968	-0.6116	-0.0065	-0.238	0.007	0	0	0	0	0	0	0	0
4	1	25.6701	19.5197	0.7514	27.5411	0.0986	0	0	0.0455	0	0.0455	0	100	0
4	2	23.653	16.9227	0.7928	29.0607	0.0984	0	0	0.0455	0	0.0455	0	100	0
4	3	22.8118	16.1844	0.6593	24.168	0.0919	0	0	0.0455	0	0.0455	0	100	0
4	4	16.4182	10.7873	0.4837	17.731	0.0754	0	0	0.0455	0	0.0455	0	100	0
4	5	14.5564	7.5137	0.4146	15.1965	0.0579	0	0	0.0455	0	0.0455	0	100	0

4	6	15.7933	9.8273	0.453	16.6027	0.0657	0	0	0.0455	0	0.0455	0	100	0
4	7	6.1716	5.3192	0.1362	4.9935	0.0244	0	0	0.0455	0	0.0455	0	100	0
4	8	7.1386	3.6867	0.1822	6.6787	0.0338	0	0	0.0455	0	0.0455	0	100	0
4	9	20.7303	13.3734	0.6248	22.9033	0.0886	0	0	0.0455	0	0.0455	0	100	0
4	10	8.9131	3.194	0.1982	7.2642	0.0334	0	0	0.0455	0	0.0455	0	100	0
4	11	1.6189	1.2404	-0.0525	-1.926	-0.0002	0	0	0.0455	0	0.0455	0	100	0
4	12	10.7432	5.782	0.2838	10.4022	0.045	0	0	0.0455	0	0.0455	0	100	0
4	13	1.5884	0.8166	-0.0105	-0.3833	0.0101	0	0	0.0455	0	0.0455	0	100	0
4	14	6.4031	3.2336	0.1734	6.3554	0.0362	0	0	0.0455	0.625	0.6705	0	100	0
4	15	15.6125	10.3811	0.4713	17.2763	0.0703	0	0.625	0.0455	0	0.6705	93.21	6.79	93.21
4	16	27.9195	15.9998	0.8541	31.3081	0.1277	0.1275	0	0	0	0.1275	0	100	0
5	1	23.5648	16.7387	0.7605	27.8743	0.1008	0	0	0.0524	0	0.0524	0	100	0
5	2	24.3053	17.3486	0.7802	28.5962	0.1046	0	0	0.0524	0	0.0524	0	100	0
5	3	22.341	15.7024	0.7107	26.0515	0.1019	0	0	0.0524	0	0.0524	0	100	0
5	4	17.6158	11.8733	0.5469	20.0479	0.0791	0	0	0.0524	0	0.0524	0	100	0
5	5	14.2387	10.1452	0.4049	14.8406	0.0574	0	0	0.0524	0	0.0524	0	100	0
5	6	15.1152	10.7747	0.4328	15.8622	0.0615	0	0	0.0524	0	0.0524	0	100	0
5	7	6.2094	5.1538	0.1363	4.9969	0.0249	0	0	0.0524	0	0.0524	0	100	0
5	8	7.6993	4.4249	0.2079	7.6192	0.0348	0	0	0.0524	0	0.0524	0	100	0
5	9	20.3032	12.9878	0.6687	24.5092	0.091	0	0	0.0524	0	0.0524	0	100	0
5	10	10.467	7.0359	0.2642	9.6824	0.0427	0	0	0.0524	0	0.0524	0	100	0
5	11	2.8488	0.9928	-0.0496	-1.8191	-0.0034	0	0	0.0524	0	0.0524	0	100	0
5	12	8.6081	4.7427	0.2975	10.9032	0.0379	0	0	0.0524	0	0.0524	0	100	0
5	13	2.4786	0.2441	-0.0353	-1.2925	0.0105	0	0	0.0524	0	0.0524	0	100	0
5	14	5.1083	3.0311	0.1416	5.192	0.0285	0	0	0.0524	0.625	0.6774	0	7.73	92.27
5	15	11.8585	7.5495	0.3716	13.62	0.0576	0	0.625	0.0524	0	0.6774	92.27	7.73	0
5	16	0.172	0.0674	-0.0092	-0.3389	0.01	0	0	0	0	0	0	0	0
6	1	22.8548	15.2481	0.7655	28.0601	0.1096	0	0	0.0592	0	0.0592	0	100	0
6	2	25.4205	16.425	0.8006	29.3446	0.11	0	0	0.0592	0	0.0592	0	100	0
6	3	25.0359	16.7118	0.7742	28.379	0.1081	0	0	0.0592	0	0.0592	0	100	0

6	4	19.8242	13.56	0.6037	22.1285	0.0864	0	0	0.0592	0	0.0592	0	100	0
6	5	15.5667	10.9252	0.4506	16.5181	0.0668	0	0	0.0592	0	0.0592	0	100	0
6	6	14.9248	9.1668	0.4848	17.7684	0.0716	0	0	0.0592	0	0.0592	0	100	0
6	7	6.2748	4.0969	0.1824	6.6868	0.0317	0	0	0.0592	0	0.0592	0	100	0
6	8	8.4858	5.8883	0.251	9.2019	0.0404	0	0	0.0592	0	0.0592	0	100	0
6	9	21.0027	12.7923	0.7581	27.7862	0.1015	0	0	0.0592	0	0.0592	0	100	0
6	10	4.1864	1.0991	0.2231	8.177	0.044	0	0	0.0592	0	0.0592	0	100	0
6	11	-1.2373	-1.4393	0.0135	0.4931	0.0092	0	0	0.0592	0	0.0592	0	100	0
6	12	10.6286	6.8786	0.3149	11.5433	0.0492	0	0	0.0592	0	0.0592	0	100	0
6	13	1.0716	0.1767	0.0081	0.2959	0.0131	0	0	0.0592	0	0.0592	0	100	0
6	14	6.6959	4.4786	0.1742	6.3849	0.0291	0	0	0.0592	0.625	0.6842	0	8.65	91.35
6	15	14.9263	8.9373	0.4504	16.5076	0.0691	0	0.625	0.0592	0	0.6842	91.35	8.65	0
6	16	0.9734	0.524	-0.0068	-0.2476	0.0095	0	0	0	0	0	0	0	0
7	1	22.5418	15.4759	0.726	26.6121	0.0978	0	0	0.066	0	0.066	0	100	0
7	2	25.3352	17.1813	0.8109	29.7233	0.1123	0	0	0.066	0	0.066	0	100	0
7	3	25.4575	17.3091	0.7912	29.0012	0.1094	0	0	0.066	0	0.066	0	100	0
7	4	20.6572	14.3391	0.6313	23.1392	0.0896	0	0	0.066	0	0.066	0	100	0
7	5	15.932	11.3449	0.4504	16.51	0.0654	0	0	0.066	0	0.066	0	100	0
7	6	15.7862	11.3444	0.4701	17.2316	0.0672	0	0	0.066	0	0.066	0	100	0
7	7	6.5518	5.4328	0.1609	5.8983	0.0264	0	0	0.066	0	0.066	0	100	0
7	8	8.798	5.7477	0.2274	8.3369	0.0394	0	0	0.066	0	0.066	0	100	0
7	9	23.0075	15.3925	0.6659	24.4074	0.0863	0	0	0.066	0	0.066	0	100	0
7	10	9.2334	7.3996	0.2983	10.934	0.0356	0	0	0.066	0	0.066	0	100	0
7	11	0.7033	0.897	-0.0323	-1.1825	0.0007	0	0	0.066	0	0.066	0	100	0
7	12	9.8812	6.9932	0.3106	11.3832	0.047	0	0	0.066	0	0.066	0	100	0
7	13	1.8315	1.5281	-0.0004	-0.0142	0.0064	0	0	0.066	0	0.066	0	100	0
7	14	5.9233	4.0164	0.1346	4.9347	0.024	0	0	0.066	0.625	0.691	0	9.55	90.45
7	15	11.3981	7.0352	0.3499	12.8255	0.0508	0	0.625	0.066	0	0.691	90.45	9.55	0
7	16	26.5669	16.7815	0.8474	31.0624	0.1182	0.1275	0	0	0	0.1275	0	100	0
8	1	22.7201	15.0948	0.694	25.4388	0.0942	0	0	0.0729	0	0.0729	0	100	0

8	2	25.5968	16.5345	0.8165	29.9286	0.1106	0	0	0.0729	0	0.0729	0	100	0
8	3	26.9015	16.5093	0.8118	29.7556	0.1132	0	0	0.0729	0	0.0729	0	100	0
8	4	22.6912	14.399	0.6735	24.6849	0.0922	0	0	0.0729	0	0.0729	0	100	0
8	5	16.1513	10.0868	0.4873	17.8622	0.0711	0	0	0.0729	0	0.0729	0	100	0
8	6	14.9604	9.3549	0.5104	18.7093	0.0788	0	0	0.0729	0	0.0729	0	100	0
8	7	9.1106	4.8845	0.1351	4.9537	0.0227	0	0	0.0729	0	0.0729	0	100	0
8	8	11.6445	4.2759	0.265	9.7129	0.0431	0	0	0.0729	0	0.0729	0	100	0
8	9	22.1496	13.0101	0.7517	27.5537	0.103	0	0	0.0729	0	0.0729	0	100	0
8	10	10.7574	7.0805	0.323	11.8395	0.0477	0	0	0.0729	0	0.0729	0	100	0
8	11	3.6004	0.9577	0.0383	1.4029	0.0094	0	0	0.0729	0	0.0729	0	100	0
8	12	11.534	7.8883	0.3533	12.9484	0.0508	0	0	0.0729	0	0.0729	0	100	0
8	13	1.3464	0.5169	-0.0012	-0.0457	0.0054	0	0	0.0729	0	0.0729	0	100	0
8	14	6.4094	3.371	0.1695	6.2144	0.0276	0	0	0.0729	0.625	0.6979	0	10.44	89.56
8	15	12.8137	8.3353	0.3838	14.067	0.054	0	0.625	0.0729	0	0.6979	89.56	10.44	0
8	16	0.6005	0.7618	-0.0245	-0.8983	0.0023	0	0	0	0	0	0	0	0
9	1	22.4957	14.7378	0.6826	25.0193	0.0926	0	0	0.0797	0	0.0797	0	100	0
9	2	25.986	17.2218	0.8042	29.4787	0.1075	0	0	0.0797	0	0.0797	0	100	0
9	3	26.7278	17.0659	0.8299	30.4191	0.1155	0	0	0.0797	0	0.0797	0	100	0
9	4	21.7825	14.3953	0.6911	25.3306	0.0965	0	0	0.0797	0	0.0797	0	100	0
9	5	17.2508	11.3087	0.5012	18.3711	0.0717	0	0	0.0797	0	0.0797	0	100	0
9	6	16.9581	10.5872	0.4639	17.0022	0.0651	0	0	0.0797	0	0.0797	0	100	0
9	7	6.3335	4.0566	0.1665	6.1027	0.0326	0	0	0.0797	0	0.0797	0	100	0
9	8	11.9448	6.8015	0.2794	10.2426	0.0347	0	0	0.0797	0	0.0797	0	100	0
9	9	22.3682	14.3068	0.6953	25.4874	0.0927	0	0	0.0797	0	0.0797	0	100	0
9	10	10.6395	6.5727	0.3015	11.0498	0.0426	0	0	0.0797	0	0.0797	0	100	0
9	11	0.7463	-0.5268	-0.0297	-1.0885	0.0037	0	0	0.0797	0	0.0797	0	100	0
9	12	11.6436	6.9032	0.3308	12.1271	0.0465	0	0	0.0797	0	0.0797	0	100	0
9	13	2.2734	1.3731	-0.0036	-0.1307	0.0063	0	0	0.0797	0	0.0797	0	100	0
9	14	5.2473	2.3383	0.133	4.8766	0.0256	0	0	0.0797	0.625	0.7047	0	11.31	88.69
9	15	14.1744	8.1484	0.4386	16.0753	0.0629	0	0.625	0.0797	0	0.7047	88.69	11.31	0

9	16	1.1167	0.6406	-0.0074	-0.2708	0.0074	0	0	0	0	0	0	0	0	0	0	0	0	0
10	1	21.0706	14.7112	0.6846	25.0928	0.0968	0	0	0.0865	0	0.0865	0	0.0865	0	0.0865	0	0.0865	0	100
10	2	26.8869	17.9825	0.8859	32.4724	0.1184	0	0	0.0865	0	0.0865	0	0.0865	0	0.0865	0	0.0865	0	100
10	3	26.6813	16.9521	0.9023	33.0744	0.1263	0	0	0.0865	0	0.0865	0	0.0865	0	0.0865	0	0.0865	0	100
10	4	22.8526	14.0275	0.7543	27.65	0.106	0	0	0.0865	0	0.0865	0	0.0865	0	0.0865	0	0.0865	0	100
10	5	16.4643	9.638	0.5121	18.772	0.0768	0	0	0.0865	0	0.0865	0	0.0865	0	0.0865	0	0.0865	0	100
10	6	16.974	10.2305	0.4989	18.2853	0.0738	0	0	0.0865	0	0.0865	0	0.0865	0	0.0865	0	0.0865	0	100
10	7	7.0764	3.7892	0.217	7.954	0.0367	0	0	0.0865	0	0.0865	0	0.0865	0	0.0865	0	0.0865	0	100
10	8	10.3301	7.0156	0.3079	11.2846	0.0444	0	0	0.0865	0	0.0865	0	0.0865	0	0.0865	0	0.0865	0	100
10	9	22.9265	14.8712	0.7519	27.5603	0.1024	0	0	0.0865	0	0.0865	0	0.0865	0	0.0865	0	0.0865	0	100
10	10	12.4677	6.9963	0.3574	13.1014	0.0529	0	0	0.0865	0	0.0865	0	0.0865	0	0.0865	0	0.0865	0	100
10	11	0.5969	-0.5299	-0.0215	-0.7876	0.0033	0	0	0.0865	0	0.0865	0	0.0865	0	0.0865	0	0.0865	0	100
10	12	13.3324	8.0107	0.3981	14.593	0.0579	0	0	0.0865	0	0.0865	0	0.0865	0	0.0865	0	0.0865	0	100
10	13	1.9031	0.5698	0.0129	0.4715	0.0076	0	0	0.0865	0	0.0865	0	0.0865	0	0.0865	0	0.0865	0	100
10	14	6.4847	3.7801	0.156	5.7172	0.0292	0	0	0.0865	0.625	0.0865	0.625	0.0865	0.625	0.0865	0.625	0.0865	0.625	12.16
10	15	13.3979	8.7146	0.4385	16.0738	0.0621	0	0.625	0.0865	0	0.0865	0	0.0865	0	0.0865	0	0.0865	0	12.16
10	16	25.4495	16.0477	0.8342	30.5766	0.1176	0	0.1275	0	0	0	0	0	0	0.1275	0	0	0	100
11	1	20.1375	13.3902	0.695	25.4752	0.0941	0	0	0.0933	0	0.0933	0	0.0933	0	0.0933	0	0.0933	0	100
11	2	27.139	17.1786	0.8841	32.4048	0.1236	0	0	0.0933	0	0.0933	0	0.0933	0	0.0933	0	0.0933	0	100
11	3	26.9388	16.683	0.9125	33.4483	0.127	0	0	0.0933	0	0.0933	0	0.0933	0	0.0933	0	0.0933	0	100
11	4	24.5762	15.8875	0.789	28.9207	0.1089	0	0	0.0933	0	0.0933	0	0.0933	0	0.0933	0	0.0933	0	100
11	5	15.1923	9.882	0.4773	17.4944	0.0718	0	0	0.0933	0	0.0933	0	0.0933	0	0.0933	0	0.0933	0	100
11	6	15.7362	10.517	0.4959	18.1782	0.0704	0	0	0.0933	0	0.0933	0	0.0933	0	0.0933	0	0.0933	0	100
11	7	6.9524	4.547	0.2149	7.8771	0.0338	0	0	0.0933	0	0.0933	0	0.0933	0	0.0933	0	0.0933	0	100
11	8	10.7228	5.8543	0.3063	11.2265	0.0473	0	0	0.0933	0	0.0933	0	0.0933	0	0.0933	0	0.0933	0	100
11	9	21.6871	13.7234	0.7381	27.0563	0.1017	0	0	0.0933	0	0.0933	0	0.0933	0	0.0933	0	0.0933	0	100
11	10	10.2552	6.749	0.3273	11.9961	0.0462	0	0	0.0933	0	0.0933	0	0.0933	0	0.0933	0	0.0933	0	100
11	11	0.1751	-0.8137	-0.0162	-0.5948	0.0093	0	0	0.0933	0	0.0933	0	0.0933	0	0.0933	0	0.0933	0	100
11	12	12.9233	7.3461	0.3959	14.5118	0.058	0	0	0.0933	0	0.0933	0	0.0933	0	0.0933	0	0.0933	0	100
11	13	2.1161	-0.0461	0.0196	0.7173	0.0121	0	0	0.0933	0	0.0933	0	0.0933	0	0.0933	0	0.0933	0	100

11	14	5.318	2.5839	0.1421	5.2076	0.028	0	0	0.0933	0.625	0.7183	0	12.99	87.01
11	15	12.7569	6.3017	0.3941	14.4456	0.0579	0	0.625	0.0933	0	0.7183	87.01	12.99	0
11	16	0.8455	-1.3583	0.0027	0.0985	0.0084	0	0	0	0	0	0	0	0
12	1	15.9884	10.3576	0.5209	19.0939	0.0763	0	0	0.1002	0	0.1002	0	100	0
12	2	27.3984	16.7714	0.9241	33.8719	0.128	0	0	0.1002	0	0.1002	0	100	0
12	3	28.1625	17.4315	0.9325	34.1804	0.1313	0	0	0.1002	0	0.1002	0	100	0
12	4	24.8213	15.2594	0.851	31.1941	0.1246	0	0	0.1002	0	0.1002	0	100	0
12	5	16.5105	9.4519	0.5715	20.9463	0.089	0	0	0.1002	0	0.1002	0	100	0
12	6	16.2367	8.6629	0.5246	19.229	0.0791	0	0	0.1002	0	0.1002	0	100	0
12	7	7.0822	2.7268	0.2494	9.143	0.0433	0	0	0.1002	0	0.1002	0	100	0
12	8	11.1025	6.1665	0.3763	13.7941	0.056	0	0	0.1002	0	0.1002	0	100	0
12	9	23.5429	14.4559	0.8026	29.419	0.1129	0	0	0.1002	0	0.1002	0	100	0
12	10	12.4169	7.2141	0.384	14.0754	0.0576	0	0	0.1002	0	0.1002	0	100	0
12	11	-0.2192	-1.5288	-0.0114	-0.4195	0.0063	0	0	0.1002	0	0.1002	0	100	0
12	12	13.2567	7.0496	0.4182	15.3281	0.0611	0	0	0.1002	0	0.1002	0	100	0
12	13	1.2187	-0.6308	0.0286	1.0496	0.0116	0	0	0.1002	0	0.1002	0	100	0
12	14	5.5276	1.9229	0.1649	6.0426	0.0328	0	0	0.1002	0.625	0.7252	86.19	13.81	86.19
12	15	13.3469	6.2659	0.4232	15.5137	0.0634	0	0.625	0.1002	0	0.7252	86.19	13.81	0
12	16	1.0083	-0.586	0.011	0.4039	0.0096	0	0	0	0	0	0	0	0
13	1	18.6644	11.2964	0.6506	23.8458	0.0932	0	0	0.107	0	0.107	0	100	0
13	2	27.845	15.9413	0.9392	34.4261	0.1308	0	0	0.107	0	0.107	0	100	0
13	3	27.3697	17.3186	0.9442	34.6097	0.1337	0	0	0.107	0	0.107	0	100	0
13	4	25.678	15.9207	0.8401	30.7915	0.1183	0	0	0.107	0	0.107	0	100	0
13	5	15.7945	10.0005	0.5228	19.164	0.0793	0	0	0.107	0	0.107	0	100	0
13	6	15.3463	9.2398	0.5087	18.6471	0.0765	0	0	0.107	0	0.107	0	100	0
13	7	6.7754	3.6609	0.2308	8.459	0.0396	0	0	0.107	0	0.107	0	100	0
13	8	11.692	6.4553	0.3752	13.7513	0.0561	0	0	0.107	0	0.107	0	100	0
13	9	23.2809	13.521	0.8112	29.7353	0.1124	0	0	0.107	0	0.107	0	100	0
13	10	13.5562	7.5286	0.4302	15.7676	0.0624	0	0	0.107	0	0.107	0	100	0
13	11	1.1357	-1.0497	-0.0258	-0.9457	0.0072	0	0	0.107	0	0.107	0	100	0

13	12	14.0892	7.0847	0.4404	16.1411	0.0683	0	0	0	0.107	0	0.107	0	100	0
13	13	1.2307	-0.0972	0.0411	1.5048	0.0161	0	0	0	0.107	0	0.107	0	100	0
13	14	5.0473	1.1814	0.1519	5.5685	0.0306	0	0	0	0.107	0.625	0.732	0	14.62	85.38
13	15	12.8894	6.9657	0.3932	14.413	0.0574	0	0	0.625	0.107	0	0.732	85.38	14.62	0
13	16	27.0196	15.8321	0.9126	33.449	0.1349	0.1275	0	0	0	0	0.1275	0	100	0
14	1	21.6824	14.5808	0.7642	28.0108	0.1054	0	0	0	0.1138	0	0.1138	0	100	0
14	2	27.9534	18.5673	0.9122	33.4357	0.1269	0	0	0	0.1138	0	0.1138	0	100	0
14	3	28.3871	17.6025	0.9506	34.8433	0.1361	0	0	0	0.1138	0	0.1138	0	100	0
14	4	26.5322	15.1329	0.8627	31.6204	0.1283	0	0	0	0.1138	0	0.1138	0	100	0
14	5	17.27	10.4633	0.5486	20.1091	0.0846	0	0	0	0.1138	0	0.1138	0	100	0
14	6	16.6826	9.6418	0.5721	20.9704	0.0848	0	0	0	0.1138	0	0.1138	0	100	0
14	7	7.7667	4.5307	0.2694	9.8752	0.0433	0	0	0	0.1138	0	0.1138	0	100	0
14	8	13.2575	8.5866	0.4374	16.0317	0.064	0	0	0	0.1138	0	0.1138	0	100	0
14	9	24.5972	16.2327	0.8255	30.2566	0.1118	0	0	0	0.1138	0	0.1138	0	100	0
14	10	14.1237	8.1483	0.478	17.5191	0.0713	0	0	0	0.1138	0	0.1138	0	100	0
14	11	-0.172	-1.5106	-0.0204	-0.7482	0.0089	0	0	0	0.1138	0	0.1138	0	100	0
14	12	15.8277	8.9664	0.5076	18.6043	0.0706	0	0	0	0.1138	0	0.1138	0	100	0
14	13	1.0637	-1.0104	0.0444	1.6268	0.0139	0	0	0	0.1138	0	0.1138	0	100	0
14	14	4.6635	2.3532	0.1677	6.1462	0.0296	0	0	0	0.1138	0.625	0.7388	0	15.41	84.59
14	15	12.9488	7.3298	0.4296	15.7453	0.0651	0	0	0.625	0.1138	0	0.7388	84.59	15.41	0
14	16	0.3061	-0.5069	-0.0065	-0.2391	0.0099	0	0	0	0	0	0	0	0	0
15	1	17.1998	12.0104	0.5755	21.0955	0.0799	0	0	0	0.1207	0	0.1207	0	100	0
15	2	27.4482	17.526	0.933	34.1967	0.1316	0	0	0	0.1207	0	0.1207	0	100	0
15	3	28.1178	18.8556	0.9242	33.8763	0.1324	0	0	0	0.1207	0	0.1207	0	100	0
15	4	26.8701	17.1463	0.856	31.3778	0.1258	0	0	0	0.1207	0	0.1207	0	100	0
15	5	17.6631	10.9667	0.5845	21.4248	0.0858	0	0	0	0.1207	0	0.1207	0	100	0
15	6	17.1402	10.8854	0.5425	19.8853	0.0798	0	0	0	0.1207	0	0.1207	0	100	0
15	7	8.2663	5.3027	0.2441	8.9487	0.0387	0	0	0	0.1207	0	0.1207	0	100	0
15	8	11.9892	6.7241	0.3904	14.3081	0.0566	0	0	0	0.1207	0	0.1207	0	100	0
15	9	24.1606	15.639	0.8291	30.3902	0.1118	0	0	0	0.1207	0	0.1207	0	100	0

15	10	15.0377	10.3936	0.4614	16.9136	0.0638	0	0	0.1207	0	0.1207	0	100	0
15	11	0.2191	-0.9933	-0.0152	-0.558	0.0074	0	0	0.1207	0	0.1207	0	100	0
15	12	16.1138	9.1228	0.5094	18.6707	0.0732	0	0	0.1207	0	0.1207	0	100	0
15	13	2.4821	0.3422	0.0309	1.1317	0.0144	0	0	0.1207	0	0.1207	0	100	0
15	14	5.4454	0.6463	0.189	6.9276	0.035	0	0	0.1207	0.625	0.7457	0	16.18	83.82
15	15	14.0229	7.8558	0.4492	16.4654	0.0681	0	0.625	0.1207	0	0.7457	83.82	16.18	0
15	16	0.4686	-0.7131	0.0197	0.7216	0.01	0	0	0	0	0	0	0	0
16	1	7.4861	4.4402	0.2493	9.1386	0.0401	0	0	0.1275	0	0.1275	0	100	0
16	2	29.0506	17.8613	0.9483	34.7579	0.1412	0	0	0.1275	0	0.1275	0	100	0
16	3	29.4694	17.4993	0.9236	33.8554	0.1479	0	0	0.1275	0	0.1275	0	100	0
16	4	28.4749	16.4322	0.9104	33.3693	0.1531	0	0	0.1275	0	0.1275	0	100	0
16	5	22.0326	12.6858	0.7055	25.8606	0.1115	0	0	0.1275	0	0.1275	0	100	0
16	6	20.0805	12.1402	0.6291	23.0594	0.0943	0	0	0.1275	0	0.1275	0	100	0
16	7	9.0587	5.2161	0.2666	9.7703	0.0461	0	0	0.1275	0	0.1275	0	100	0
16	8	13.983	9.3075	0.4391	16.0948	0.0636	0	0	0.1275	0	0.1275	0	100	0
16	9	26.9905	17.0719	0.877	32.1456	0.1198	0	0	0.1275	0	0.1275	0	100	0
16	10	14.704	8.6762	0.4886	17.9102	0.073	0	0	0.1275	0	0.1275	0	100	0
16	11	0.7191	-1.4742	-0.0041	-0.1519	0.0077	0	0	0.1275	0	0.1275	0	100	0
16	12	19.314	11.1355	0.6495	23.808	0.0899	0	0	0.1275	0	0.1275	0	100	0
16	13	2.4636	0.033	0.0679	2.4886	0.0206	0	0	0.1275	0	0.1275	0	100	0
16	14	11.4461	6.8975	0.3856	14.134	0.0639	0	0	0.1275	0.625	0.7525	0	16.94	83.06
16	15	20.8264	13.1623	0.7	25.6595	0.0961	0	0.625	0.1275	0	0.7525	83.06	16.94	0
16	16	26.7851	15.9945	0.9048	33.1661	0.1319	0.1275	0	0	0	0.1275	0	100	0
Temperature: 300C														
1	1	26.0412	13.6761	0.7608	27.4327	0.1592	0.1275	0	0	0	0.1275	0	100	0
1	2	1.9716	2.4686	0.0066	0.2386	0.0092	0	0	0	0	0	0	0	0
1	3	0.3229	0.3952	-0.0391	-1.4081	0.0062	0	0	0	0	0	0	0	0
1	4	0.6417	0.8578	-0.0504	-1.8187	-0.0005	0	0	0	0	0	0	0	0
1	5	0.173	0.5233	-0.0449	-1.6183	0.0024	0	0	0	0	0	0	0	0

1	6	0.3624	0.0747	-0.0376	-1.3546	-0.0039	0	0	0	0	0	0	0	0
1	7	26.157	12.3934	0.797	28.7383	0.1699	0.1275	0	0	0	0.1275	0	100	0
1	8	3.5333	0.2801	-0.0585	-2.108	-0.0107	0	0	0	0	0	0	0	0
1	9	-1.8657	-3.8002	-0.0104	-0.375	0.0197	0	0	0	0	0	0	0	0
1	10	2.592	0.129	-0.014	-0.5051	-0.0253	0	0	0	0	0	0	0	0
1	11	-3.1613	-1.397	-0.0273	-0.9858	0.0043	0	0	0	0	0	0	0	0
1	12	-0.5382	-0.741	-0.0195	-0.7042	-0.0352	0	0	0	0	0	0	0	0
1	13	25.293	12.9331	0.8097	29.194	0.1597	0.1275	0	0	0	0.1275	0	100	0
1	14	0.8774	0.3654	-0.018	-0.648	0.0052	0	0	0	0	0	0	0	0
1	15	-1.2793	0.1383	-0.0181	-0.6543	0.0027	0	0	0	0	0	0	0	0
1	16	25.6735	12.143	0.7277	26.2368	0.1566	0.1275	0	0	0	0.1275	0	100	0
2	1	14.8766	10.2106	0.3917	14.1217	0.0524	0	0	0.0319	0	0.0319	0	100	0
2	2	20.4545	14.6181	0.746	26.8969	0.1088	0	0	0.0319	0	0.0319	0	100	0
2	3	19.9352	12.3858	0.6977	25.1579	0.1196	0	0	0.0319	0	0.0319	0	100	0
2	4	16.0396	10.1097	0.6511	23.4768	0.109	0	0	0.0319	0	0.0319	0	100	0
2	5	15.904	10.2101	0.4597	16.5765	0.0626	0	0	0.0319	0	0.0319	0	100	0
2	6	14.9915	9.8692	0.3995	14.4034	0.0662	0	0	0.0319	0	0.0319	0	100	0
2	7	6.2101	5.2473	0.1852	6.6763	0.0252	0	0	0.0319	0	0.0319	0	100	0
2	8	9.4972	5.8339	0.283	10.205	0.0496	0	0	0.0319	0	0.0319	0	100	0
2	9	21.1669	13.9111	0.6435	23.2016	0.0932	0	0	0.0319	0	0.0319	0	100	0
2	10	8.0932	5.8934	0.2958	10.6661	0.0493	0	0	0.0319	0	0.0319	0	100	0
2	11	0.4906	0.3109	-0.0754	-2.7173	0.0004	0	0	0.0319	0	0.0319	0	100	0
2	12	12.7979	8.96	0.445	16.0439	0.0703	0	0	0.0319	0	0.0319	0	100	0
2	13	1.7683	2.1621	0.0286	1.0326	0.0176	0	0	0.0319	0	0.0319	0	100	0
2	14	11.5049	8.9483	0.3603	12.9899	0.0656	0	0	0.0319	0	0.0319	0	100	0
2	15	19.2509	11.5249	0.6541	23.5849	0.0881	0	0.625	0.0319	0	0.6569	0	4.85	95.15
2	16	-2.2275	0.1022	0.0038	0.136	0.001	0	0	0	0	0.6569	95.15	4.85	0
3	1	19.5625	13.7405	0.7553	27.2322	0.1169	0	0	0.0387	0	0.0387	0	100	0
3	2	23.3448	16.4986	0.7782	28.0599	0.1055	0	0	0.0387	0	0.0387	0	100	0
3	3	20.2746	14.4888	0.7447	26.8513	0.1236	0	0	0.0387	0	0.0387	0	100	0

3	4	21.042	14.6567	0.5975	21.5435	0.0868	0	0	0.0387	0	0.0387	0	100	0
3	5	15.227	11.3009	0.5184	18.6931	0.0896	0	0	0.0387	0	0.0387	0	100	0
3	6	16.2981	13.1574	0.4916	17.7266	0.0804	0	0	0.0387	0	0.0387	0	100	0
3	7	7.5318	7.7146	0.2177	7.8495	0.0364	0	0	0.0387	0	0.0387	0	100	0
3	8	14.1025	10.9954	0.419	15.1061	0.0628	0	0	0.0387	0	0.0387	0	100	0
3	9	20.9253	15.3432	0.7024	25.3266	0.1019	0	0	0.0387	0	0.0387	0	100	0
3	10	13.728	11.1605	0.4466	16.1033	0.0679	0	0	0.0387	0	0.0387	0	100	0
3	11	-1.0656	0.7638	-0.03	-1.0824	-0.001	0	0	0.0387	0	0.0387	0	100	0
3	12	12.0316	9.0087	0.4143	14.9372	0.064	0	0	0.0387	0	0.0387	0	100	0
3	13	2.3735	2.427	0.0472	1.7003	0.0158	0	0	0.0387	0	0.0387	0	100	0
3	14	10.011	6.6184	0.4321	15.5784	0.078	0	0	0.0387	0.625	0.6637	0	5.83	94.17
3	15	17.1288	11.9418	0.6936	25.0081	0.1016	0	0.625	0.0387	0	0.6637	94.17	5.83	0
3	16	-0.0207	-0.0056	0.0564	2.0341	-0.003	0	0	0	0	0	0	0	0
4	1	23.9972	15.9845	0.7717	27.8233	0.119	0	0	0.0455	0	0.0455	0	100	0
4	2	24.3635	16.2531	0.7072	25.5007	0.1199	0	0	0.0455	0	0.0455	0	100	0
4	3	21.4425	14.1432	0.7498	27.0362	0.1265	0	0	0.0455	0	0.0455	0	100	0
4	4	19.4479	12.996	0.6822	24.5996	0.107	0	0	0.0455	0	0.0455	0	100	0
4	5	16.0527	11.3163	0.5819	20.98	0.0935	0	0	0.0455	0	0.0455	0	100	0
4	6	17.5309	11.186	0.5671	20.447	0.0842	0	0	0.0455	0	0.0455	0	100	0
4	7	8.0993	5.7381	0.3374	12.166	0.0503	0	0	0.0455	0	0.0455	0	100	0
4	8	14.119	9.8107	0.5489	19.7929	0.0801	0	0	0.0455	0	0.0455	0	100	0
4	9	23.2762	14.9011	0.7786	28.0723	0.1033	0	0	0.0455	0	0.0455	0	100	0
4	10	14.7194	10.4363	0.5718	20.6185	0.08	0	0	0.0455	0	0.0455	0	100	0
4	11	1.1453	0.3882	-0.067	-2.4162	-0.0168	0	0	0.0455	0	0.0455	0	100	0
4	12	12.7656	8.8311	0.4759	17.1582	0.0689	0	0	0.0455	0	0.0455	0	100	0
4	13	4.4502	1.323	0.0072	0.2593	0.0135	0	0	0.0455	0	0.0455	0	100	0
4	14	13.3844	9.4729	0.4141	14.9311	0.0687	0	0	0.0455	0.625	0.6705	0	6.79	93.21
4	15	20.7018	14.4153	0.6795	24.5002	0.0932	0	0.625	0.0455	0	0.6705	93.21	6.79	0
4	16	26.3093	12.5646	0.7405	26.6988	0.1561	0.1275	0	0	0	0.1275	0	100	0
5	1	21.4105	14.4067	0.7125	25.6898	0.11	0	0	0.0524	0	0.0524	0	100	0

5	2	22.1022	14.8036	0.819	29.5304	0.1282	0	0	0.0524	0	0.0524	0	100	0
5	3	22.5933	14.8442	0.7244	26.1201	0.1233	0	0	0.0524	0	0.0524	0	100	0
5	4	21.0057	13.8057	0.6911	24.9201	0.1153	0	0	0.0524	0	0.0524	0	100	0
5	5	17.672	12.2393	0.5728	20.6522	0.0902	0	0	0.0524	0	0.0524	0	100	0
5	6	16.0245	11.7967	0.5902	21.2789	0.0941	0	0	0.0524	0	0.0524	0	100	0
5	7	8.682	6.8022	0.35	12.6185	0.0569	0	0	0.0524	0	0.0524	0	100	0
5	8	16.2047	10.7313	0.5656	20.3921	0.0857	0	0	0.0524	0	0.0524	0	100	0
5	9	21.0729	14.0649	0.7974	28.7515	0.124	0	0	0.0524	0	0.0524	0	100	0
5	10	18.1655	12.1093	0.6249	22.5323	0.094	0	0	0.0524	0	0.0524	0	100	0
5	11	-3.2789	-1.8833	0.0173	0.625	-0.017	0	0	0.0524	0	0.0524	0	100	0
5	12	12.1376	7.6528	0.5085	18.3339	0.0689	0	0	0.0524	0	0.0524	0	100	0
5	13	2.8719	1.6064	0.0398	1.4347	0.0232	0	0	0.0524	0	0.0524	0	100	0
5	14	11.6313	7.1984	0.3756	13.5442	0.064	0	0	0.0524	0.625	0.6774	0	7.73	92.27
5	15	18.7077	12.3422	0.6784	24.4596	0.1017	0	0.625	0.0524	0	0.6774	92.27	7.73	0
5	16	-0.923	0.6423	0.0024	0.0871	-0.0005	0	0	0	0	0	0	0	0
6	1	22.0063	14.1082	0.7772	28.0216	0.121	0	0	0.0592	0	0.0592	0	100	0
6	2	23.7522	14.4251	0.8181	29.4983	0.1363	0	0	0.0592	0	0.0592	0	100	0
6	3	23.7349	12.7968	0.778	28.0518	0.1487	0	0	0.0592	0	0.0592	0	100	0
6	4	21.7688	12.1769	0.7488	27.0006	0.1335	0	0	0.0592	0	0.0592	0	100	0
6	5	18.6185	12.368	0.6292	22.6862	0.1057	0	0	0.0592	0	0.0592	0	100	0
6	6	17.435	11.7025	0.6457	23.2833	0.0997	0	0	0.0592	0	0.0592	0	100	0
6	7	9.5496	7.4033	0.4005	14.4418	0.0656	0	0	0.0592	0	0.0592	0	100	0
6	8	18.8345	12.608	0.602	21.7077	0.0895	0	0	0.0592	0	0.0592	0	100	0
6	9	22.7783	14.5707	0.7858	28.3319	0.1268	0	0	0.0592	0	0.0592	0	100	0
6	10	14.2889	9.3319	0.4808	17.3344	0.0626	0	0	0.0592	0	0.0592	0	100	0
6	11	-1.4423	-3.1898	0.0072	0.2597	-0.0242	0	0	0.0592	0	0.0592	0	100	0
6	12	14.6391	9.1343	0.5169	18.6393	0.0784	0	0	0.0592	0	0.0592	0	100	0
6	13	1.3924	0.1849	0.1067	3.8458	0.0254	0	0	0.0592	0	0.0592	0	100	0
6	14	12.4467	7.9011	0.47	16.947	0.0796	0	0	0.0592	0.625	0.6842	0	8.65	91.35
6	15	20.5551	12.4877	0.7241	26.1085	0.1086	0	0.625	0.0592	0	0.6842	91.35	8.65	0

6	16	1.8224	1.9194	0.0293	1.0577	-0.001	0	0	0	0	0	0	0	0	0
7	1	20.1793	13.5157	0.7141	25.7483	0.1062	0	0	0.066	0	0.066	0	0.066	0	100
7	2	23.9199	15.0715	0.7923	28.5691	0.1334	0	0	0.066	0	0.066	0	0.066	0	100
7	3	24.0921	13.8724	0.7704	27.7794	0.1489	0	0	0.066	0	0.066	0	0.066	0	100
7	4	22.4883	13.3333	0.7472	26.9401	0.1331	0	0	0.066	0	0.066	0	0.066	0	100
7	5	18.3753	10.967	0.6933	24.9964	0.1147	0	0	0.066	0	0.066	0	0.066	0	100
7	6	19.1636	11.8882	0.594	21.4179	0.0973	0	0	0.066	0	0.066	0	0.066	0	100
7	7	11.6242	8.7829	0.358	12.9075	0.0589	0	0	0.066	0	0.066	0	0.066	0	100
7	8	18.9461	11.9304	0.6075	21.9057	0.0865	0	0	0.066	0	0.066	0	0.066	0	100
7	9	20.8727	13.268	0.8581	30.9391	0.1366	0	0	0.066	0	0.066	0	0.066	0	100
7	10	19.7469	12.533	0.627	22.6084	0.0889	0	0	0.066	0	0.066	0	0.066	0	100
7	11	0.2661	-1.0746	-0.0206	-0.7417	-0.0241	0	0	0.066	0	0.066	0	0.066	0	100
7	12	14.9635	8.7674	0.5117	18.4485	0.0776	0	0	0.066	0	0.066	0	0.066	0	100
7	13	2.473	1.1259	0.0915	3.3004	0.0134	0	0	0.066	0	0.066	0	0.066	0	100
7	14	10.4908	6.4436	0.4097	14.774	0.0771	0	0	0.066	0.625	0.691	0	0.691	90.45	90.45
7	15	17.9387	11.3159	0.7335	26.449	0.109	0	0.625	0.066	0	0.691	90.45	0.691	90.45	90.45
7	16	24.6649	12.1883	0.7892	28.4564	0.1735	0.1275	0	0	0	0.1275	0	0.1275	0	100
8	1	20.4072	13.9072	0.7031	25.3521	0.1107	0	0	0.0729	0	0.0729	0	0.0729	0	100
8	2	23.2299	15.5533	0.8078	29.1272	0.1368	0	0	0.0729	0	0.0729	0	0.0729	0	100
8	3	24.3029	13.9797	0.7799	28.1203	0.1564	0	0	0.0729	0	0.0729	0	0.0729	0	100
8	4	22.2113	14.5975	0.7495	27.0256	0.1425	0	0	0.0729	0	0.0729	0	0.0729	0	100
8	5	18.1577	13.0692	0.6943	25.034	0.1167	0	0	0.0729	0	0.0729	0	0.0729	0	100
8	6	16.4584	11.241	0.6799	24.5135	0.1128	0	0	0.0729	0	0.0729	0	0.0729	0	100
8	7	11.3178	9.6452	0.4321	15.5795	0.0596	0	0	0.0729	0	0.0729	0	0.0729	0	100
8	8	20.8336	14.4605	0.6457	23.2815	0.0922	0	0	0.0729	0	0.0729	0	0.0729	0	100
8	9	23.346	15.3942	0.8346	30.0941	0.1169	0	0	0.0729	0	0.0729	0	0.0729	0	100
8	10	20.3283	13.3467	0.6964	25.1102	0.1063	0	0	0.0729	0	0.0729	0	0.0729	0	100
8	11	6.0017	3.7447	0.2344	8.4523	0.0402	0	0	0.0729	0	0.0729	0	0.0729	0	100
8	12	14.0669	9.2173	0.572	20.6246	0.0862	0	0	0.0729	0	0.0729	0	0.0729	0	100
8	13	0.4343	-0.3379	0.1029	3.7103	0.0224	0	0	0.0729	0	0.0729	0	0.0729	0	100

8	14	12.9196	8.2041	0.4689	16.9054	0.0749	0	0	0.0729	0.625	0.6979	0	10.44	89.56
8	15	20.3025	12.6472	0.6618	23.8639	0.1	0	0.625	0.0729	0	0.6979	89.56	10.44	0
8	16	0.7273	0.7062	-0.0175	-0.63	-0.0087	0	0	0	0	0	0	0	0
9	1	19.0866	13.801	0.6956	25.0805	0.1067	0	0	0.0797	0	0.0797	0	100	0
9	2	23.4011	15.4022	0.8062	29.0677	0.1362	0	0	0.0797	0	0.0797	0	100	0
9	3	24.2636	14.0356	0.8069	29.094	0.1585	0	0	0.0797	0	0.0797	0	100	0
9	4	23.0618	13.7204	0.7603	27.4122	0.137	0	0	0.0797	0	0.0797	0	100	0
9	5	19.2953	12.3324	0.6838	24.6546	0.1191	0	0	0.0797	0	0.0797	0	100	0
9	6	16.4524	11.6941	0.5833	21.033	0.0966	0	0	0.0797	0	0.0797	0	100	0
9	7	8.8155	6.193	0.4081	14.7154	0.0678	0	0	0.0797	0	0.0797	0	100	0
9	8	18.3421	12.4823	0.6492	23.4094	0.095	0	0	0.0797	0	0.0797	0	100	0
9	9	22.5571	15.4221	0.8241	29.7153	0.1201	0	0	0.0797	0	0.0797	0	100	0
9	10	18.2863	13.1397	0.6724	24.2444	0.0988	0	0	0.0797	0	0.0797	0	100	0
9	11	-1.5339	-0.5868	-0.0006	-0.0218	-0.0198	0	0	0.0797	0	0.0797	0	100	0
9	12	13.9602	9.1693	0.5547	20.0022	0.0819	0	0	0.0797	0	0.0797	0	100	0
9	13	1.1827	1.2849	0.1107	3.9916	0.0024	0	0	0.0797	0	0.0797	0	100	0
9	14	10.2757	6.1288	0.3969	14.3106	0.0711	0	0	0.0797	0.625	0.7047	0	11.31	88.69
9	15	19.4095	11.4849	0.732	26.3918	0.1116	0	0.625	0.0797	0	0.7047	88.69	11.31	0
9	16	-0.4746	0.3	0.0649	2.3389	0.0106	0	0	0	0	0	0	0	0
10	1	19.6155	13.2592	0.7151	25.784	0.1137	0	0	0.0865	0	0.0865	0	100	0
10	2	24.4255	14.2114	0.8452	30.474	0.1541	0	0	0.0865	0	0.0865	0	100	0
10	3	25.1167	12.0723	0.8229	29.6706	0.1783	0	0	0.0865	0	0.0865	0	100	0
10	4	23.9367	12.0867	0.8302	29.934	0.1595	0	0	0.0865	0	0.0865	0	100	0
10	5	20.499	11.2772	0.6949	25.0561	0.1257	0	0	0.0865	0	0.0865	0	100	0
10	6	18.4277	10.342	0.652	23.5077	0.1136	0	0	0.0865	0	0.0865	0	100	0
10	7	10.6829	8.2331	0.4943	17.8212	0.0797	0	0	0.0865	0	0.0865	0	100	0
10	8	21.0351	13.5697	0.6934	25.0025	0.1016	0	0	0.0865	0	0.0865	0	100	0
10	9	23.3546	15.5724	0.8319	29.9961	0.1265	0	0	0.0865	0	0.0865	0	100	0
10	10	20.2733	13.206	0.7226	26.0547	0.1094	0	0	0.0865	0	0.0865	0	100	0
10	11	-2.2709	-1.6818	-0.003	-0.1081	-0.0191	0	0	0.0865	0	0.0865	0	100	0

10	12	15.5394	9.154	0.5767	20.7948	0.0875	0	0	0.0865	0	0.0865	0	100	0
10	13	2.338	0.6958	0.1166	4.204	0.0286	0	0	0.0865	0	0.0865	0	100	0
10	14	11.8371	7.0502	0.4485	16.1702	0.0781	0	0	0.0865	0.625	0.7115	0	12.16	87.84
10	15	18.9643	11.9052	0.7159	25.8125	0.1082	0	0.625	0.0865	0	0.7115	87.84	12.16	0
10	16	23.3683	12.0328	0.7792	28.0962	0.1577	0.1275	0	0	0	0.1275	0	100	0
11	1	18.6802	11.5742	0.6796	24.5045	0.1057	0	0	0.0933	0	0.0933	0	100	0
11	2	25.0222	13.9863	0.8039	28.9852	0.1512	0	0	0.0933	0	0.0933	0	100	0
11	3	25.6394	13.1215	0.8122	29.2838	0.1687	0	0	0.0933	0	0.0933	0	100	0
11	4	24.6744	14.5183	0.7802	28.132	0.1536	0	0	0.0933	0	0.0933	0	100	0
11	5	19.3295	12.6135	0.685	24.6995	0.1225	0	0	0.0933	0	0.0933	0	100	0
11	6	18.7665	11.7823	0.6491	23.4044	0.1112	0	0	0.0933	0	0.0933	0	100	0
11	7	12.0459	8.262	0.4669	16.8355	0.0746	0	0	0.0933	0	0.0933	0	100	0
11	8	19.7356	12.2924	0.7225	26.0526	0.1072	0	0	0.0933	0	0.0933	0	100	0
11	9	23.3494	14.4131	0.8518	30.7139	0.1298	0	0	0.0933	0	0.0933	0	100	0
11	10	19.1323	12.6849	0.7094	25.5779	0.105	0	0	0.0933	0	0.0933	0	100	0
11	11	-0.9895	-0.2695	-0.004	-0.1435	-0.0127	0	0	0.0933	0	0.0933	0	100	0
11	12	14.8304	10.1963	0.582	20.9867	0.0899	0	0	0.0933	0	0.0933	0	100	0
11	13	2.208	2.5587	0.1029	3.7107	0.0204	0	0	0.0933	0	0.0933	0	100	0
11	14	10.9763	6.4266	0.3918	14.1258	0.0707	0	0	0.0933	0.625	0.7183	0	12.99	87.01
11	15	18.1906	10.6621	0.698	25.1685	0.106	0	0.625	0.0933	0	0.7183	87.01	12.99	0
11	16	-0.9643	-0.7161	0.0392	1.4143	-0.0048	0	0	0	0	0	0	0	0
12	1	15.4588	10.1833	0.5953	21.4632	0.1001	0	0	0.1002	0	0.1002	0	100	0
12	2	24.7319	13.6012	0.8478	30.5688	0.161	0	0	0.1002	0	0.1002	0	100	0
12	3	26.8912	12.8758	0.8008	28.8754	0.1851	0	0	0.1002	0	0.1002	0	100	0
12	4	24.6558	12.9216	0.8196	29.5504	0.1758	0	0	0.1002	0	0.1002	0	100	0
12	5	20.5267	12.1018	0.7215	26.0139	0.1329	0	0	0.1002	0	0.1002	0	100	0
12	6	18.4287	11.4481	0.6811	24.5589	0.1172	0	0	0.1002	0	0.1002	0	100	0
12	7	13.4393	9.372	0.4909	17.6995	0.0793	0	0	0.1002	0	0.1002	0	100	0
12	8	21.0809	13.9911	0.7512	27.0875	0.111	0	0	0.1002	0	0.1002	0	100	0
12	9	23.772	15.0448	0.8517	30.7084	0.1339	0	0	0.1002	0	0.1002	0	100	0

12	10	19.8095	12.8912	0.7381	26.6137	0.1093	0	0	0.1002	0	0.1002	0	100	0
12	11	-1.4941	-1.399	-0.0134	-0.4846	-0.018	0	0	0.1002	0	0.1002	0	100	0
12	12	16.0743	10.6539	0.5977	21.5507	0.092	0	0	0.1002	0	0.1002	0	100	0
12	13	2.0581	1.6359	0.1105	3.986	0.0298	0	0	0.1002	0	0.1002	0	100	0
12	14	10.744	6.4761	0.4184	15.0852	0.076	0	0	0.1002	0.625	0.7252	0	13.81	86.19
12	15	18.2843	10.3265	0.6975	25.1492	0.112	0	0.625	0.1002	0	0.7252	86.19	13.81	0
12	16	-0.4083	-1.1083	0.0632	2.2805	0.02	0	0	0	0	0	0	0	0
13	1	17.3784	11.3659	0.6531	23.5471	0.1026	0	0	0.107	0	0.107	0	100	0
13	2	24.8735	13.9698	0.8645	31.1714	0.1634	0	0	0.107	0	0.107	0	100	0
13	3	26.731	13.2379	0.8304	29.9397	0.1799	0	0	0.107	0	0.107	0	100	0
13	4	25.0125	13.3208	0.8199	29.5626	0.1706	0	0	0.107	0	0.107	0	100	0
13	5	20.9959	12.5637	0.7	25.2389	0.1263	0	0	0.107	0	0.107	0	100	0
13	6	19.7859	13.0643	0.6384	23.0182	0.1112	0	0	0.107	0	0.107	0	100	0
13	7	12.7701	8.6484	0.4737	17.0786	0.0821	0	0	0.107	0	0.107	0	100	0
13	8	19.9798	12.3643	0.7421	26.7561	0.1113	0	0	0.107	0	0.107	0	100	0
13	9	23.9004	15.4262	0.8368	30.1725	0.1326	0	0	0.107	0	0.107	0	100	0
13	10	20.1688	14.395	0.7685	27.7093	0.1134	0	0	0.107	0	0.107	0	100	0
13	11	-1.5531	-0.2131	0.0003	0.0093	-0.0139	0	0	0.107	0	0.107	0	100	0
13	12	16.261	10.9519	0.6007	21.66	0.0928	0	0	0.107	0	0.107	0	100	0
13	13	2.1579	1.7026	0.1307	4.7131	0.0287	0	0	0.107	0	0.107	0	100	0
13	14	10.3449	7.0881	0.4013	14.4697	0.0725	0	0	0.107	0.625	0.732	0	14.62	85.38
13	15	17.9906	12.3676	0.6892	24.8485	0.1057	0	0.625	0.107	0	0.732	85.38	14.62	0
13	16	24.9296	12.3107	0.7853	28.3135	0.1895	0.1275	0	0	0	0.1275	0	100	0
14	1	19.7006	13.895	0.7196	25.9447	0.1225	0	0	0.1138	0	0.1138	0	100	0
14	2	24.628	13.7864	0.8645	31.1715	0.1715	0	0	0.1138	0	0.1138	0	100	0
14	3	27.0603	12.7211	0.8226	29.6605	0.2007	0	0	0.1138	0	0.1138	0	100	0
14	4	24.9719	12.0514	0.83	29.9259	0.1896	0	0	0.1138	0	0.1138	0	100	0
14	5	20.0669	11.3486	0.7334	26.4431	0.1416	0	0	0.1138	0	0.1138	0	100	0
14	6	19.3148	11.3116	0.7073	25.5033	0.128	0	0	0.1138	0	0.1138	0	100	0
14	7	13.0698	9.2496	0.5178	18.6703	0.0862	0	0	0.1138	0	0.1138	0	100	0

14	8	21.4825	14.0766	0.7634	27.5263	0.1153	0	0	0	0.1138	0	0.1138	0	100	0
14	9	23.8379	15.3459	0.8607	31.0347	0.1367	0	0	0	0.1138	0	0.1138	0	100	0
14	10	21.5278	13.8928	0.7851	28.3081	0.1137	0	0	0	0.1138	0	0.1138	0	100	0
14	11	-2.1621	-1.2165	-0.0091	-0.3271	-0.0078	0	0	0	0.1138	0	0.1138	0	100	0
14	12	17.3041	11.5725	0.646	23.2923	0.0958	0	0	0	0.1138	0	0.1138	0	100	0
14	13	1.949	2.0565	0.0896	3.2302	0.028	0	0	0	0.1138	0	0.1138	0	100	0
14	14	9.3689	6.5087	0.3449	12.4353	0.0636	0	0	0	0.1138	0.625	0.7388	0	15.41	84.59
14	15	18.4324	12.0276	0.6914	24.9297	0.1067	0	0.625	0	0.1138	0	0.7388	84.59	15.41	0
14	16	-0.7558	-0.6898	0.0165	0.5934	0.0011	0	0	0	0	0	0	0	0	0
15	1	18.1472	11.9418	0.6987	25.1939	0.1082	0	0	0	0.1207	0	0.1207	0	100	0
15	2	24.7631	13.6604	0.8641	31.1563	0.1697	0	0	0	0.1207	0	0.1207	0	100	0
15	3	26.1211	11.8227	0.834	30.0705	0.2037	0	0	0	0.1207	0	0.1207	0	100	0
15	4	24.5677	11.9552	0.7923	28.5692	0.1875	0	0	0	0.1207	0	0.1207	0	100	0
15	5	20.0898	11.474	0.7193	25.9371	0.144	0	0	0	0.1207	0	0.1207	0	100	0
15	6	19.3675	11.6613	0.6822	24.5972	0.1254	0	0	0	0.1207	0	0.1207	0	100	0
15	7	12.9911	8.3415	0.5124	18.477	0.0905	0	0	0	0.1207	0	0.1207	0	100	0
15	8	19.4851	12.9013	0.711	25.6353	0.1146	0	0	0	0.1207	0	0.1207	0	100	0
15	9	23.6077	14.5462	0.8618	31.074	0.1436	0	0	0	0.1207	0	0.1207	0	100	0
15	10	21.2589	13.7735	0.7922	28.5624	0.1207	0	0	0	0.1207	0	0.1207	0	100	0
15	11	-1.3789	-1.3203	0.0019	0.0686	-0.0106	0	0	0	0.1207	0	0.1207	0	100	0
15	12	16.8366	10.3498	0.6489	23.3953	0.1014	0	0	0	0.1207	0	0.1207	0	100	0
15	13	2.5374	0.8067	0.138	4.9742	0.0357	0	0	0	0.1207	0	0.1207	0	100	0
15	14	11.1396	7.0915	0.4088	14.741	0.0773	0	0	0	0.1207	0.625	0.7457	0	16.18	83.82
15	15	17.5426	10.4944	0.7045	25.4019	0.1136	0	0.625	0	0.1207	0	0.7457	83.82	16.18	0
15	16	-0.4051	-0.4444	0.0729	2.6294	0.0112	0	0	0	0	0	0	0	0	0
16	1	15.0725	8.0994	0.5869	21.1613	0.0985	0	0	0	0.1275	0	0.1275	0	100	0
16	2	24.67	8.6858	0.7009	25.2716	0.2051	0	0	0	0.1275	0	0.1275	0	100	0
16	3	27.4278	6.3099	0.707	25.4923	0.2645	0	0	0	0.1275	0	0.1275	0	100	0
16	4	24.8032	6.1186	0.6967	25.1217	0.2372	0	0	0	0.1275	0	0.1275	0	100	0
16	5	20.9479	7.854	0.6707	24.1843	0.1784	0	0	0	0.1275	0	0.1275	0	100	0

16	6	19.4346	9.972	0.6893	24.8548	0.1408	0	0	0.1275	0	0.1275	0	100	0
16	7	14.3144	8.9315	0.5183	18.6864	0.0889	0	0	0.1275	0	0.1275	0	100	0
16	8	20.6449	13.6205	0.7023	25.3217	0.1142	0	0	0.1275	0	0.1275	0	100	0
16	9	24.2561	14.785	0.854	30.7919	0.1506	0	0	0.1275	0	0.1275	0	100	0
16	10	21.0486	14.0733	0.6995	25.2209	0.1084	0	0	0.1275	0	0.1275	0	100	0
16	11	-2.2759	-0.0846	0.0413	1.4879	0.024	0	0	0.1275	0	0.1275	0	100	0
16	12	17.1423	10.7518	0.5869	21.1613	0.0898	0	0	0.1275	0	0.1275	0	100	0
16	13	3.0092	2.0883	0.2069	7.4586	0.0432	0	0	0.1275	0	0.1275	0	100	0
16	14	12.8714	7.6083	0.5142	18.5415	0.1069	0	0	0.1275	0.625	0.7525	0	16.94	83.06
16	15	17.5841	9.9481	0.6294	22.6946	0.129	0	0.625	0.1275	0	0.7525	83.06	16.94	0
16	16	25.0686	11.1805	0.8288	29.884	0.1822	0.1275	0	0	0	0.1275	0	100	0

WHAT WE CLAIM IS:

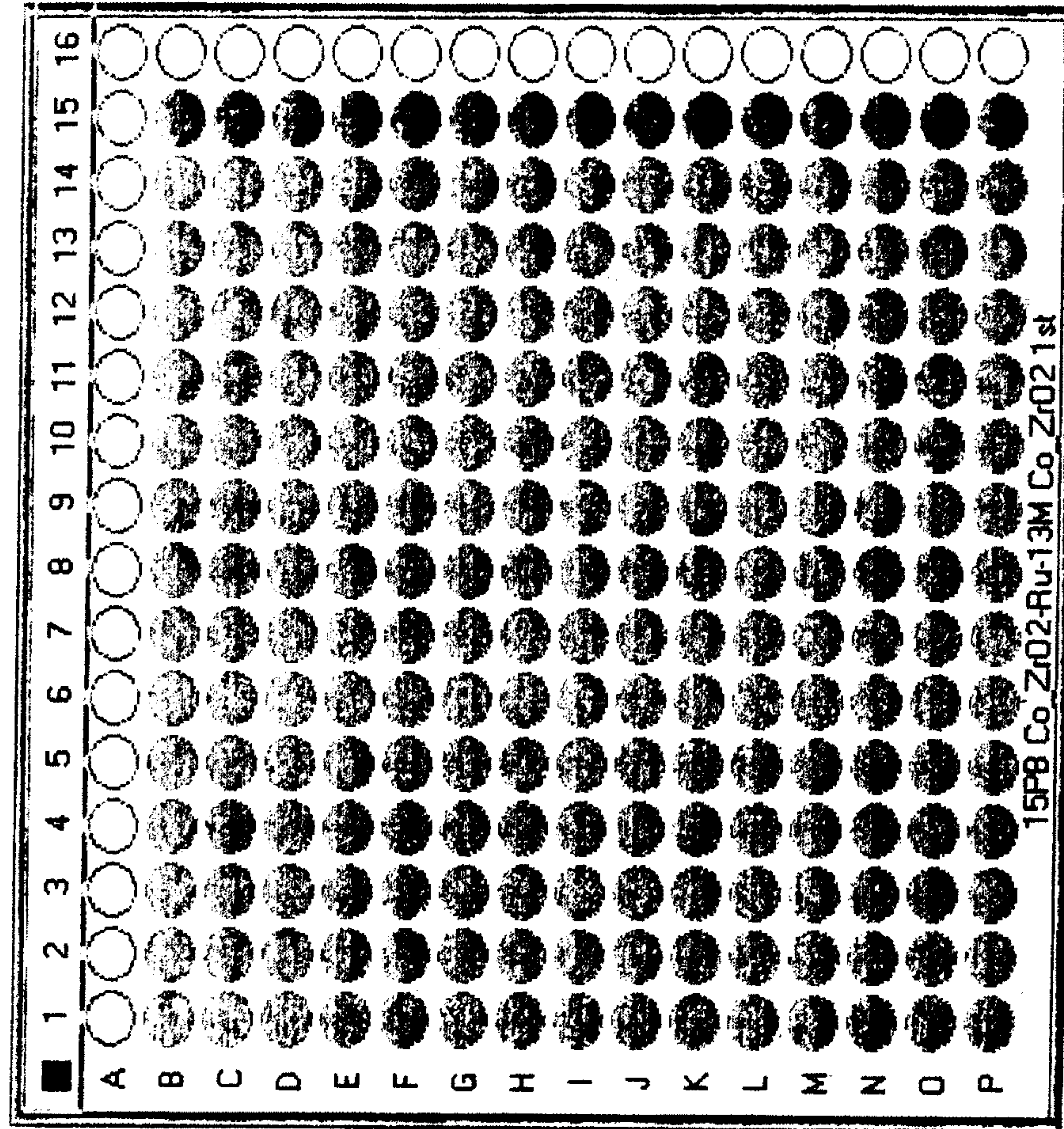
1. A catalyst for catalyzing the water gas shift reaction consisting essentially of:
 - a) Ru, its oxides or mixtures thereof;
 - b) Co, its oxides or mixtures thereof; and
 - c) Mo, its oxides or mixtures thereof;
 wherein the catalyst has an essential absence of Pt.
2. A catalyst according to claim 1, wherein the catalyst is supported on a carrier comprising at least one member selected from the group consisting of alumina, zirconia, titania, ceria, magnesia, lanthania, niobia, zeolite, perovskite, silica clay, yttria, iron oxide and mixtures thereof.
3. A catalyst according to claim 2, wherein the carrier comprises at least one member selected from the group consisting of zirconia, titania and ceria.
4. A catalyst according to claim 1, wherein the supported water gas shift catalyst comprises between about 0.01 wt. % to about 10 wt. % with respect to the total weight of all catalyst components plus the support material, of each of Ru, and Co, respectively, in the water gas shift catalyst.
5. A catalyst according to claim 1, wherein the water gas shift catalyst comprises between about 0.05 wt. % to about 20 wt. % with respect to the total weight of all catalyst components plus the support material, of each of Ru, Co, and Mo, respectively in the water gas shift catalyst.
6. A catalyst for catalyzing the water gas shift reaction consisting essentially of:
 - a) Ru, its oxides or mixtures thereof;
 - b) Co, its oxides or mixtures thereof;
 - c) Mo, its oxides or mixtures thereof; and
 - d) at least one of Li, Na, Rb, Cs, Ti, Zr, Cr, Fe, La, Ce, Eu, their oxides and mixtures thereof,
 wherein the catalyst has an essential absence of Pt.
7. A catalyst according to claim 6, wherein the catalyst is supported on a carrier comprising at least one member selected from the group consisting of alumina, zirconia, titania, ceria, magnesia, lanthania, niobia, zeolite, perovskite, silica clay, yttria, iron oxide and mixtures thereof.

8. A catalyst according to claim 7, wherein the carrier comprises at least one member selected from the group consisting of zirconia, titania and ceria.

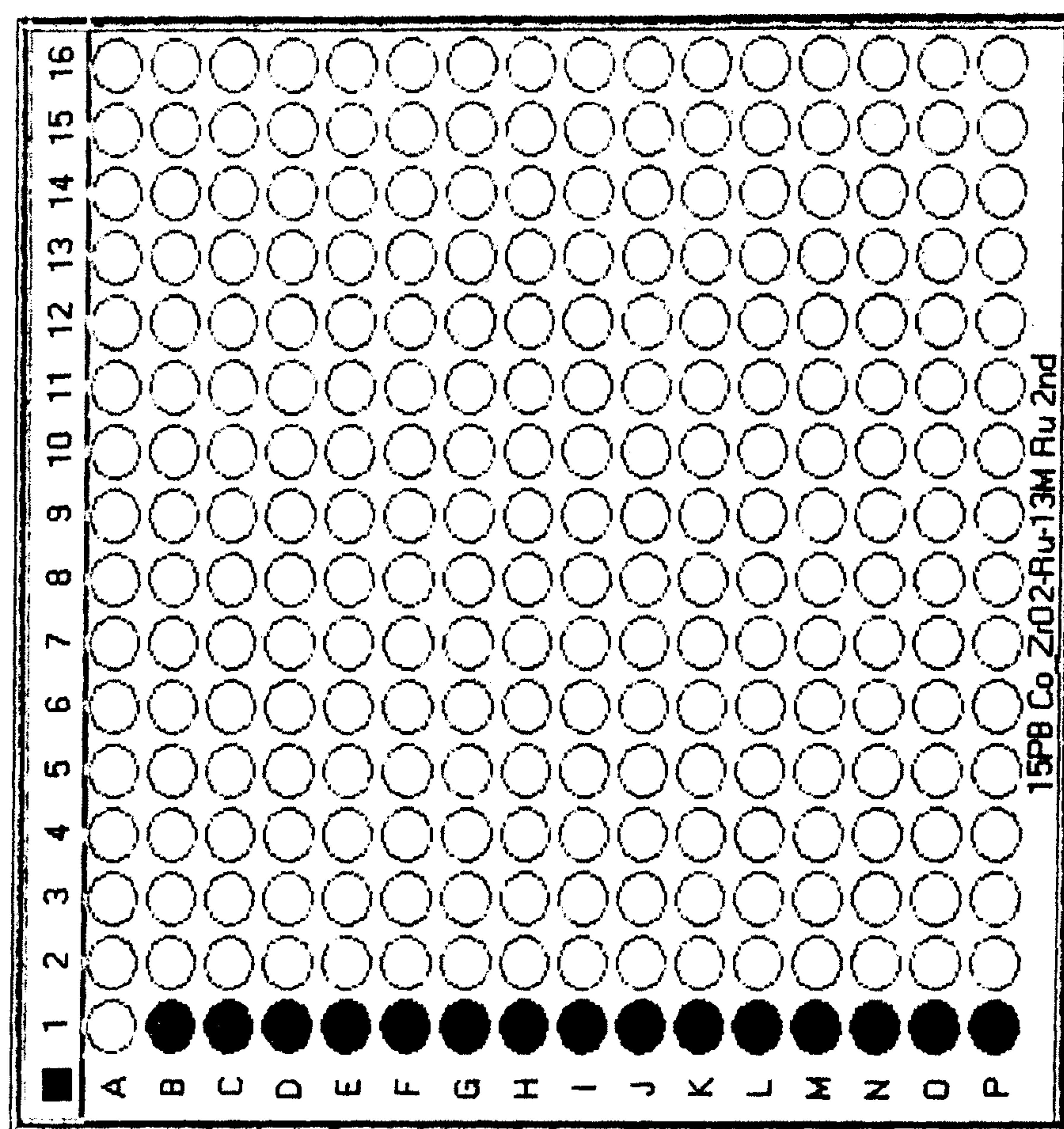
9. A catalyst according to claim 6, wherein the supported water gas shift catalyst comprises between about 0.01 wt. % to about 10 wt. % with respect to the total weight of all catalyst components plus the support material, of each of Ru and Co, respectively, in the water gas shift catalyst.

10. A catalyst according to claim 6, wherein the water gas shift catalyst comprises between about 0.05 wt. % to about 20 wt. % with respect to the total weight of all catalyst components plus the support material, of each of Ru, Co, Mo, Ti, Zr, Cr, Fe, La, Ce and Eu, respectively, present in the water gas shift catalyst.

1/43



2/43



3/43

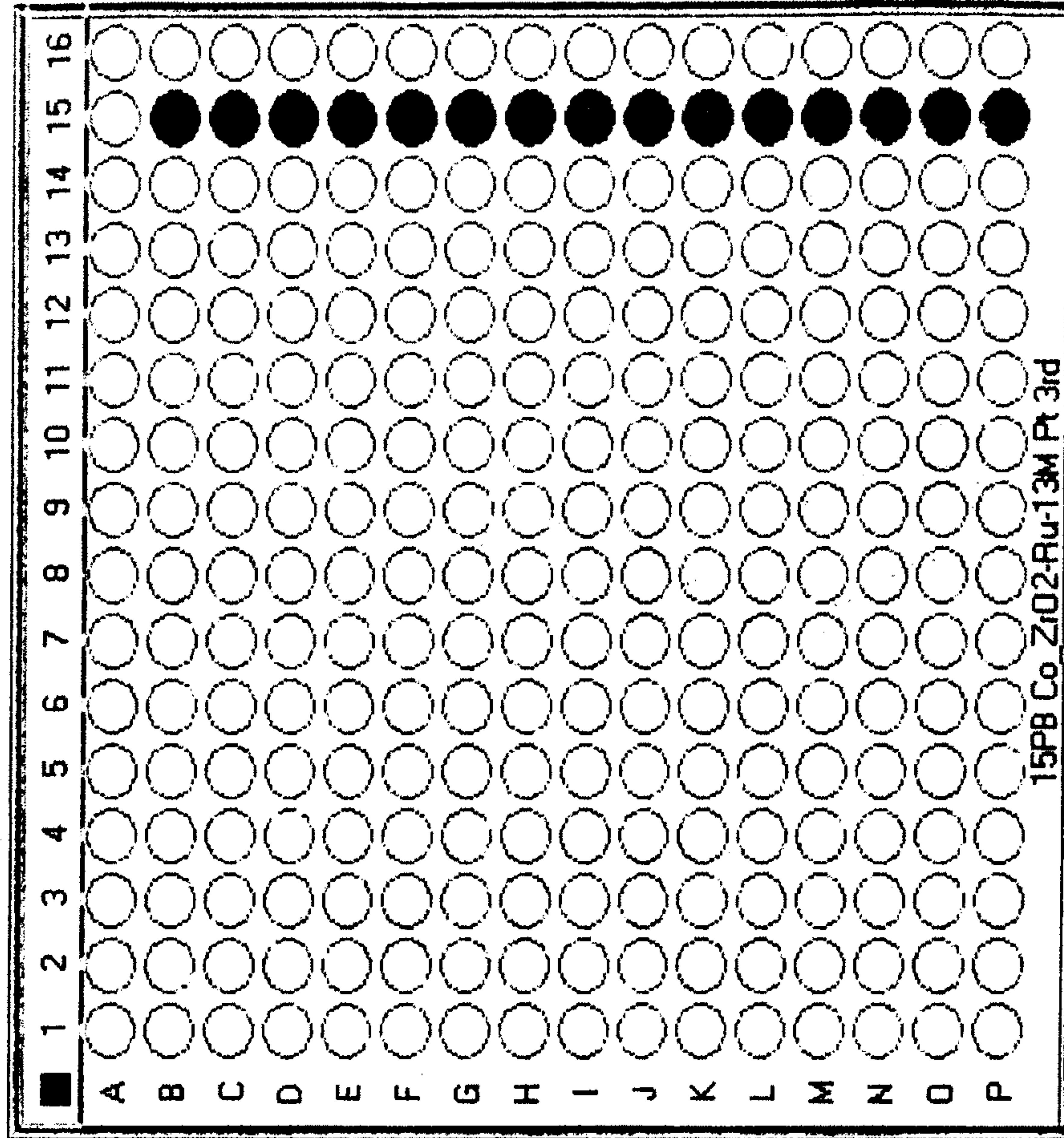


FIG. 1 C

4/43

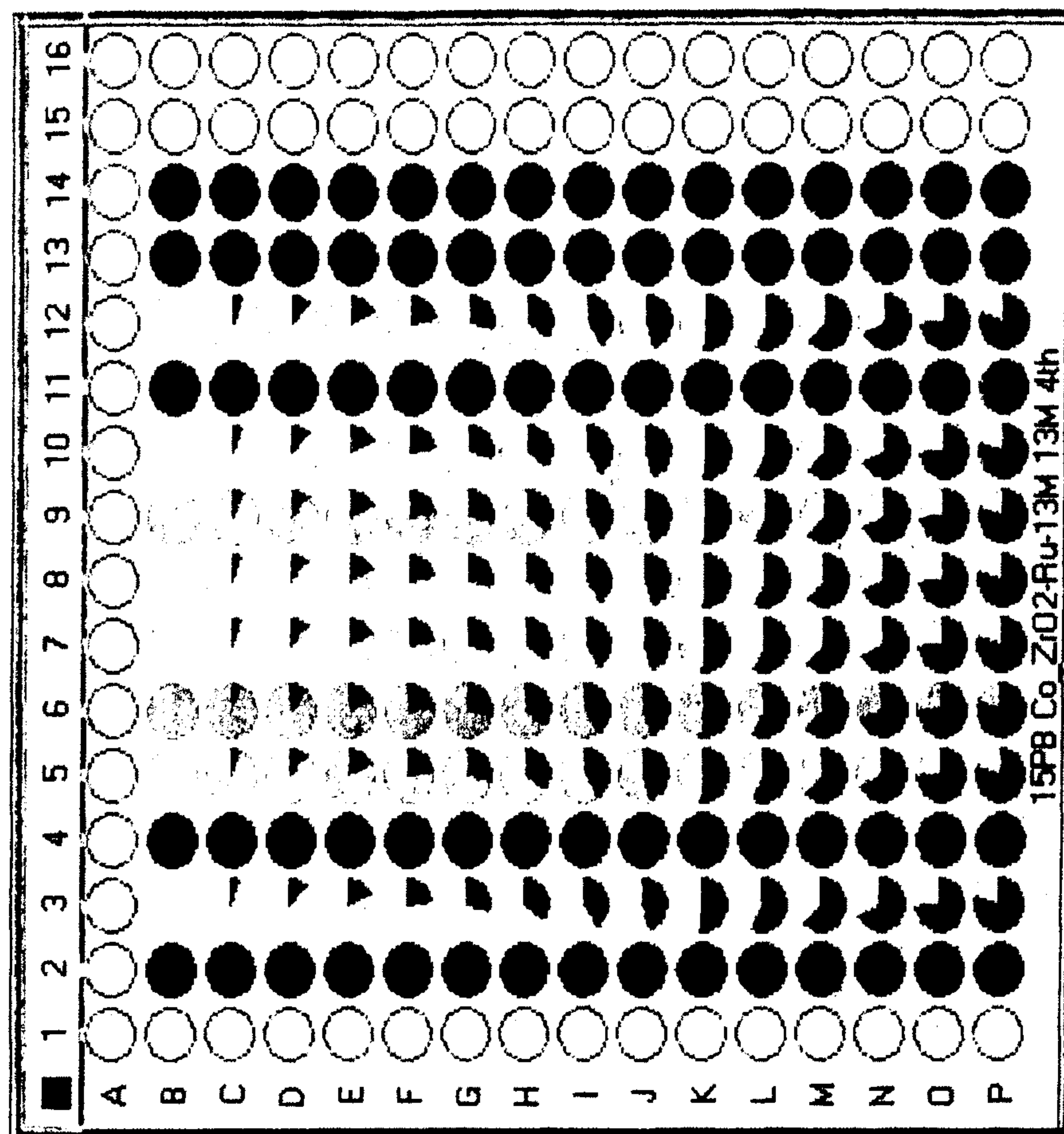


FIG. 1 D

5/43

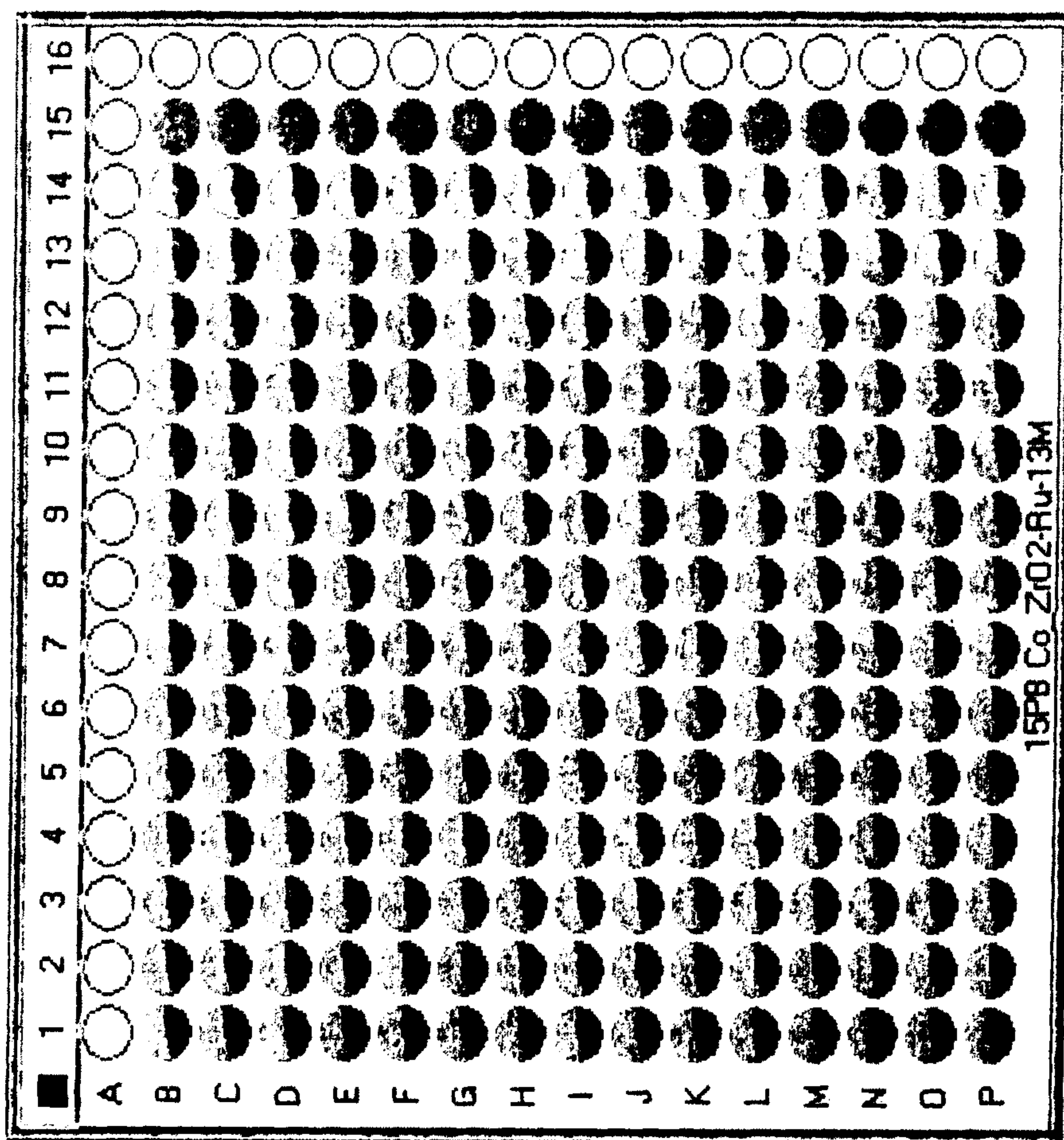
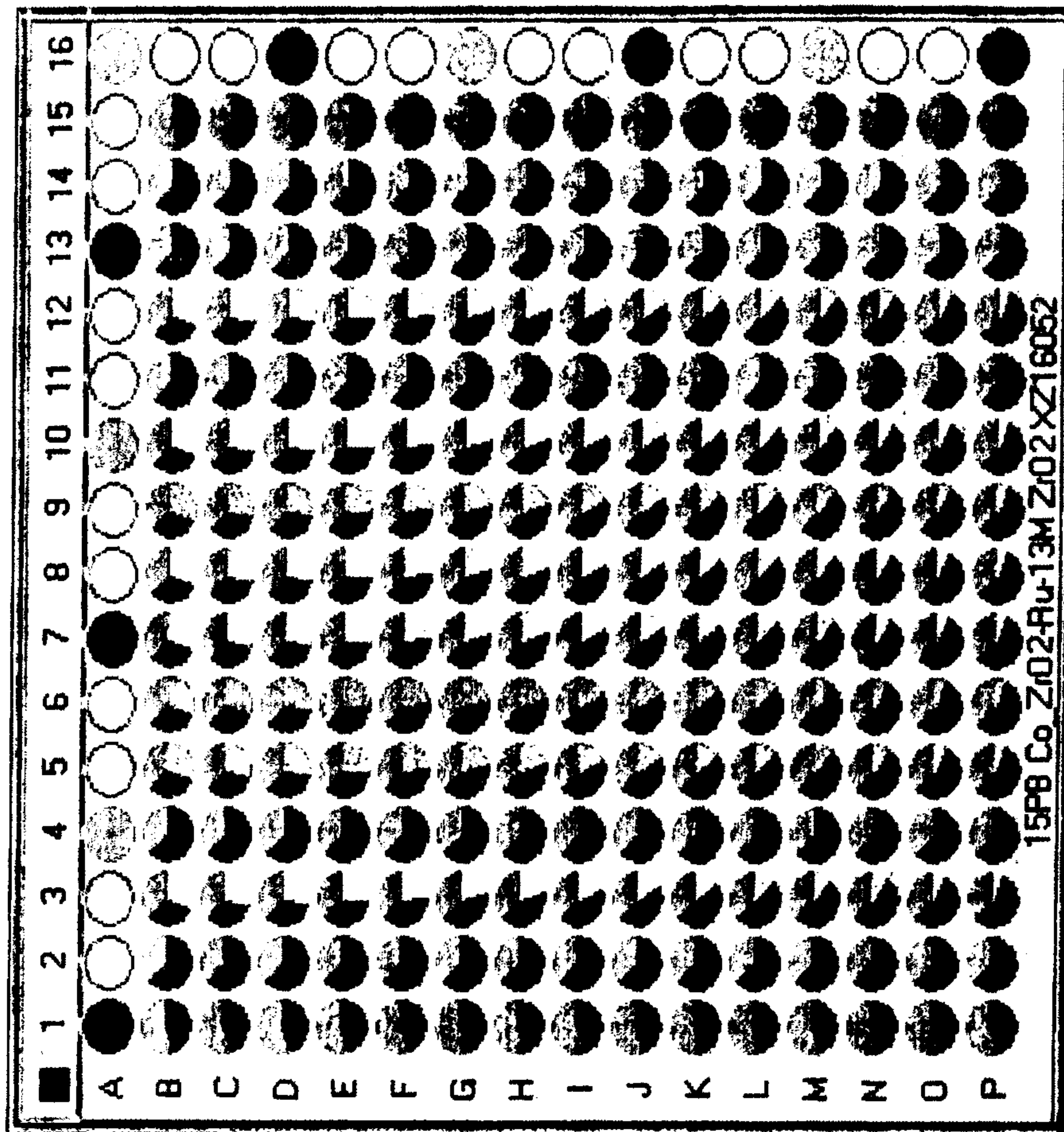


FIG. 1 E

6/43

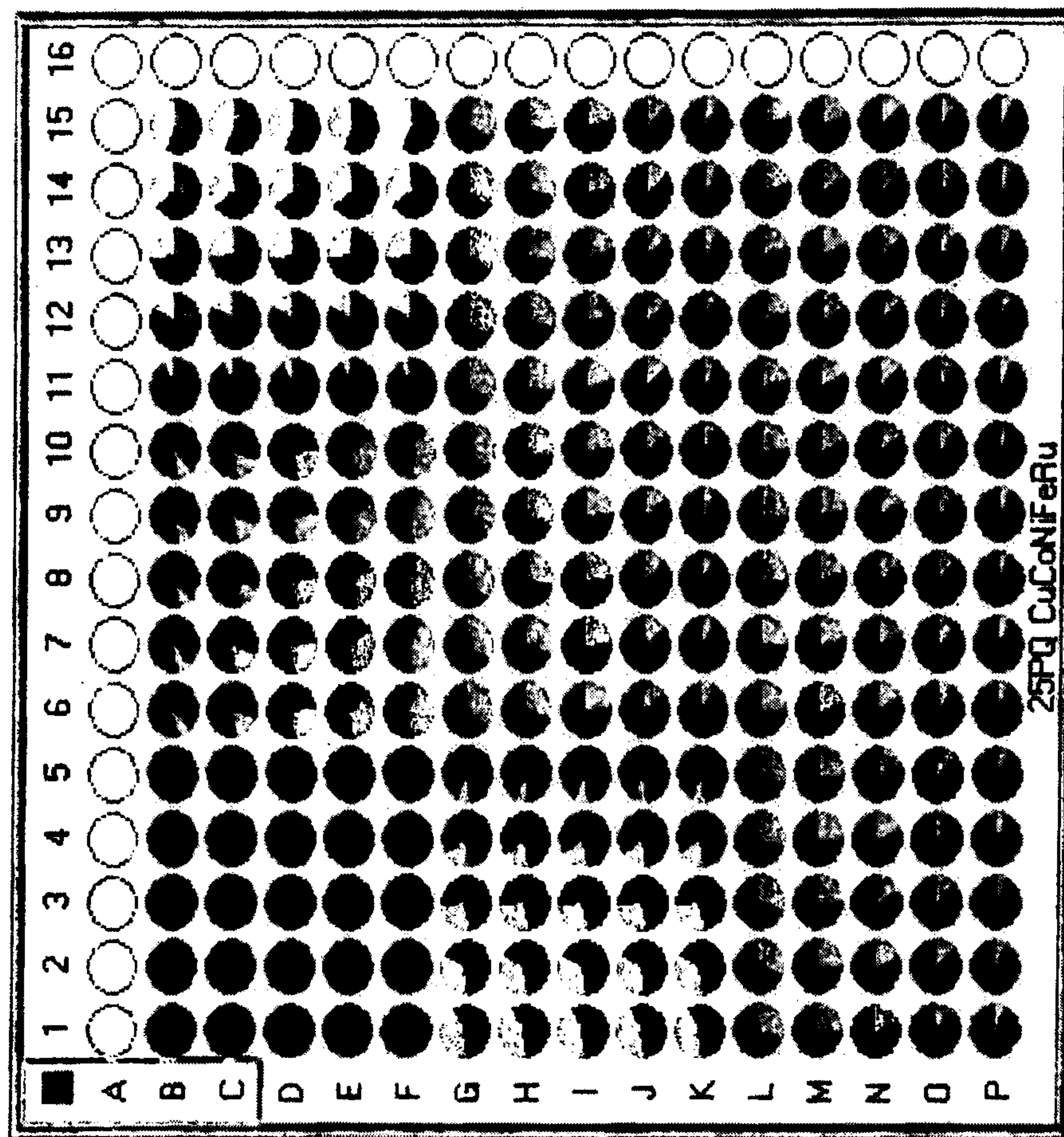


Legend:

Pt2.5%/ZrO2 std-s
 shift2 std-s
 Engelhard Co-164-s
 ZrO2-s
 RuNO33_1.5%
 H2O
 LiOH_1M
 KOH_1M
 NaOH_1M
 RbOH_1M
 FeNO33_0.25M
 H2MoO4_0.25M
 CeNO33_0.25M
 LaNO33_0.25M
 H2IrCl6_1%
 CuNO32_0.1M
 MnNO32_0.25M
 PdNH32NO22_1%
 PtNH32NO22 (unstabilized)_1%

FIG. 1 F

7/43



8/43

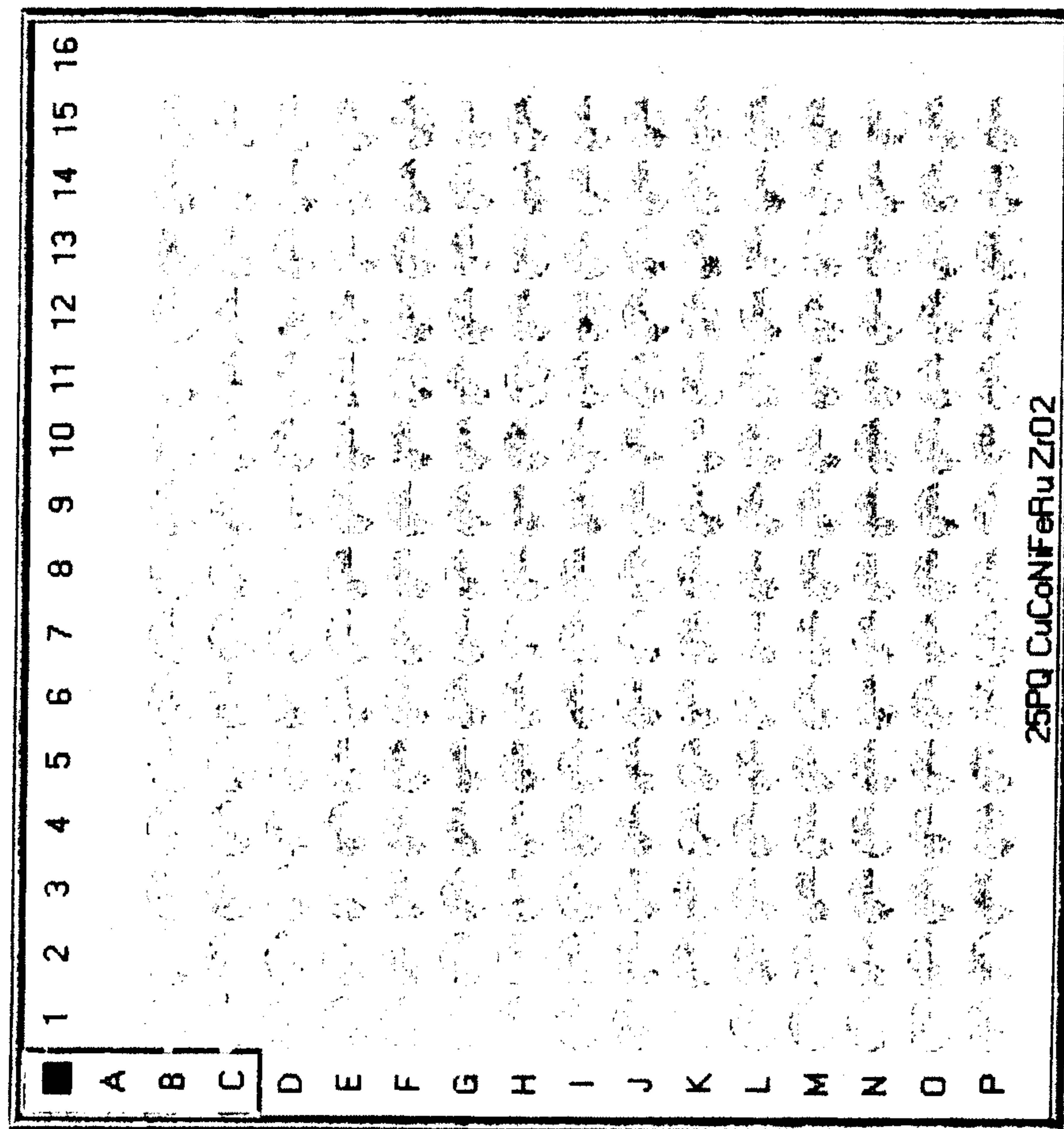
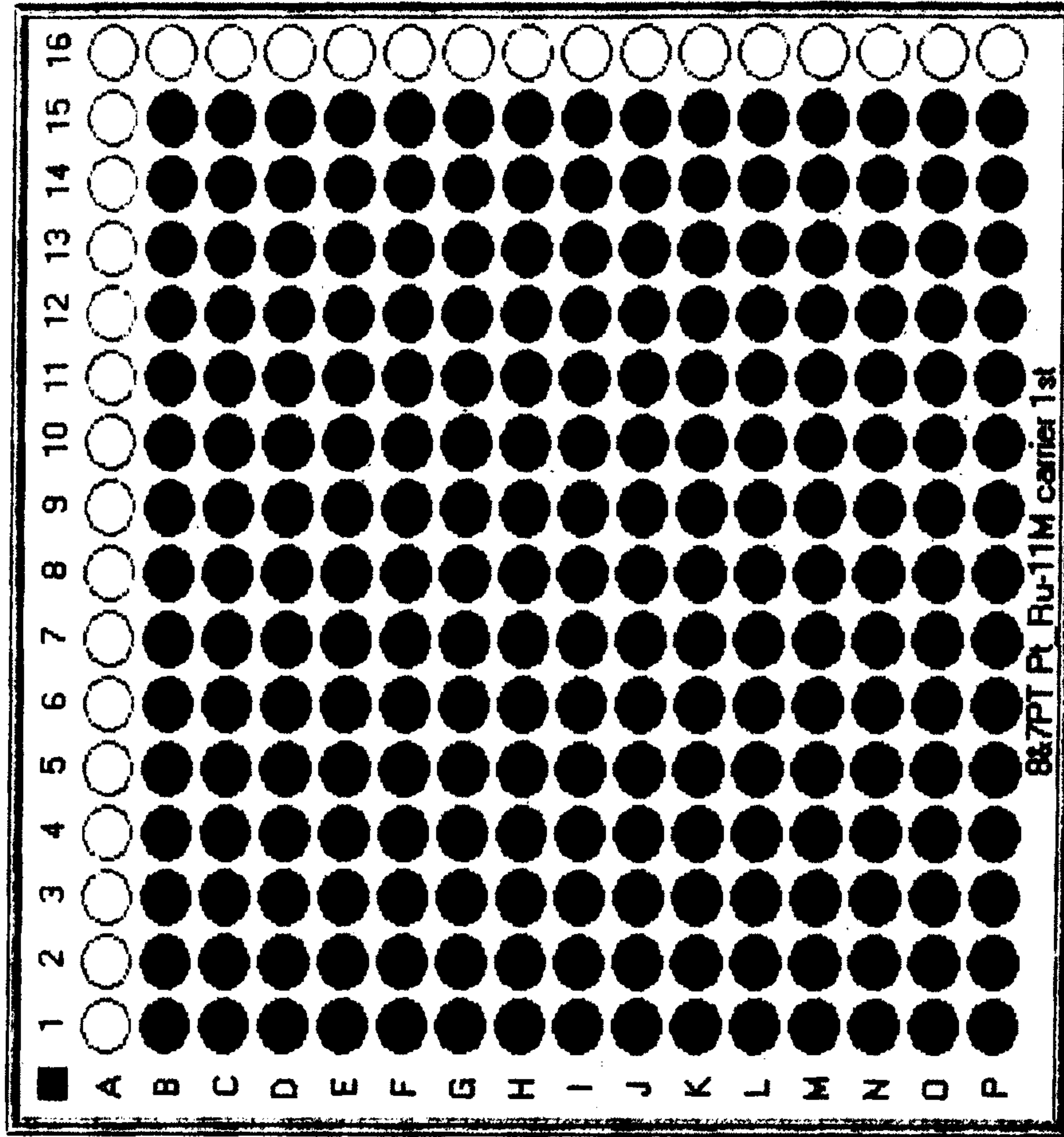


FIG. 2 B

9/43



Legend:
● Zirconia-carrier ex ZrO₂ XZ16052-s

FIG. 3 A

10/43

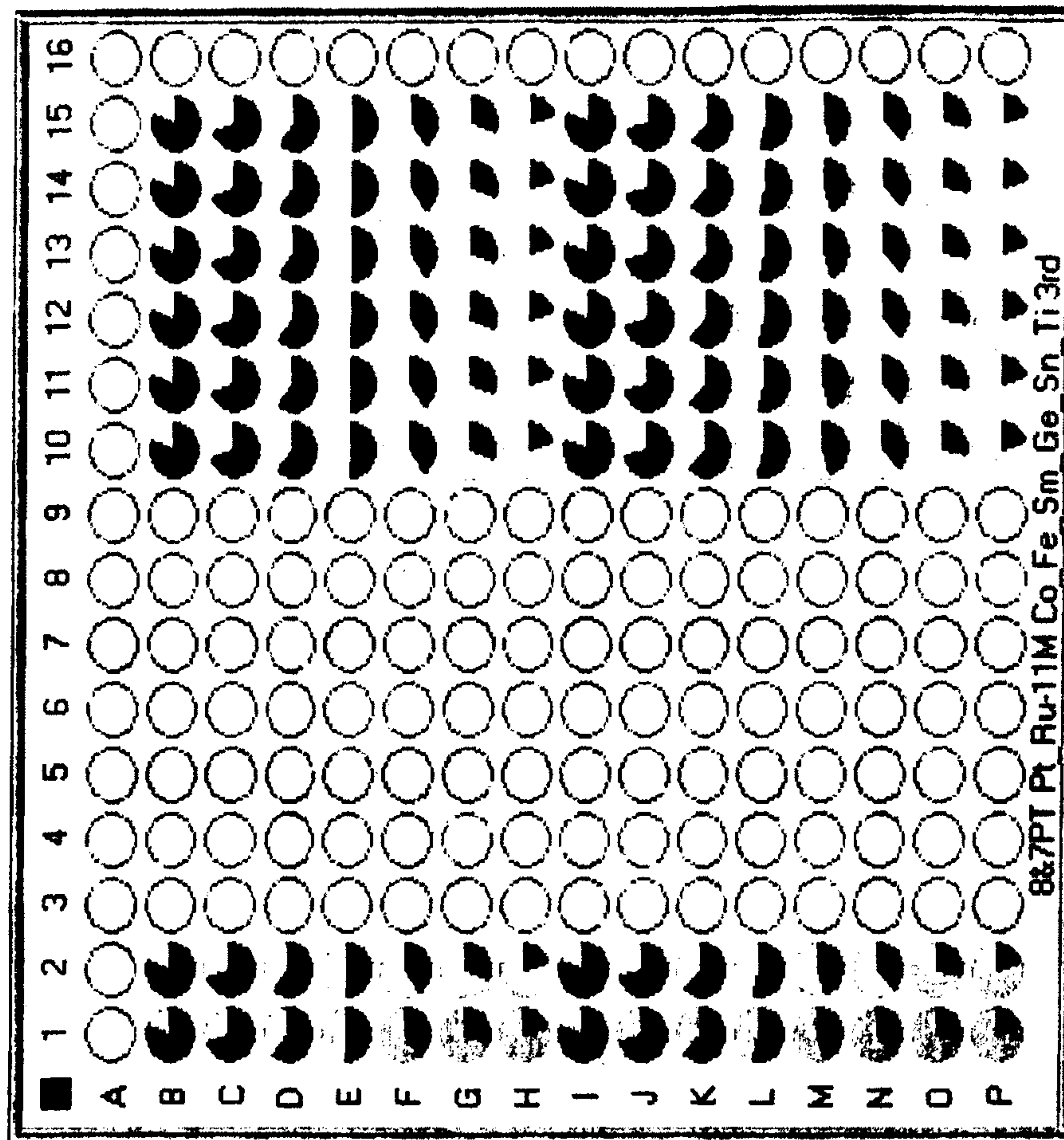


FIG. 3 B

11/43

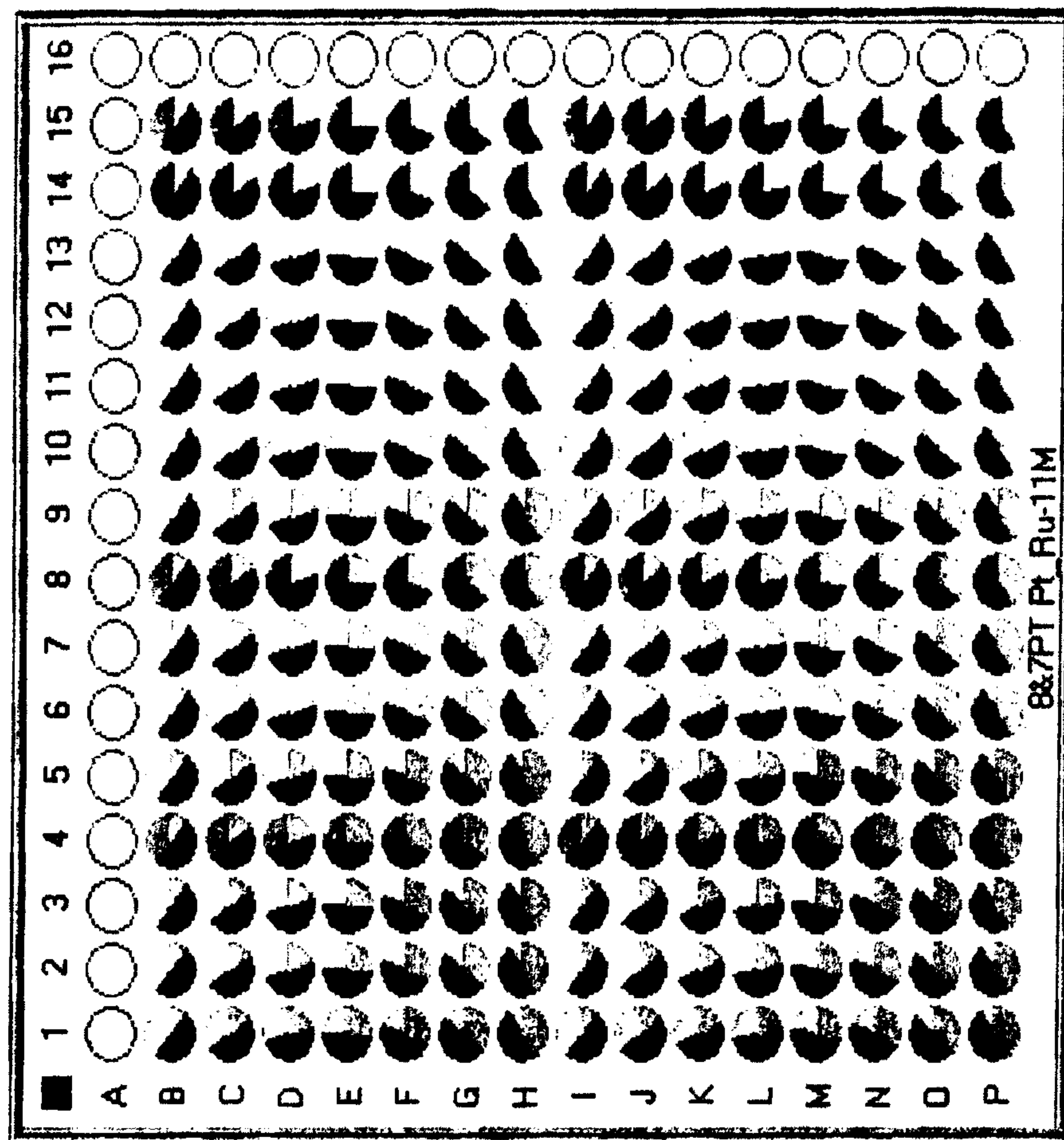


FIG. 3 C

12/43

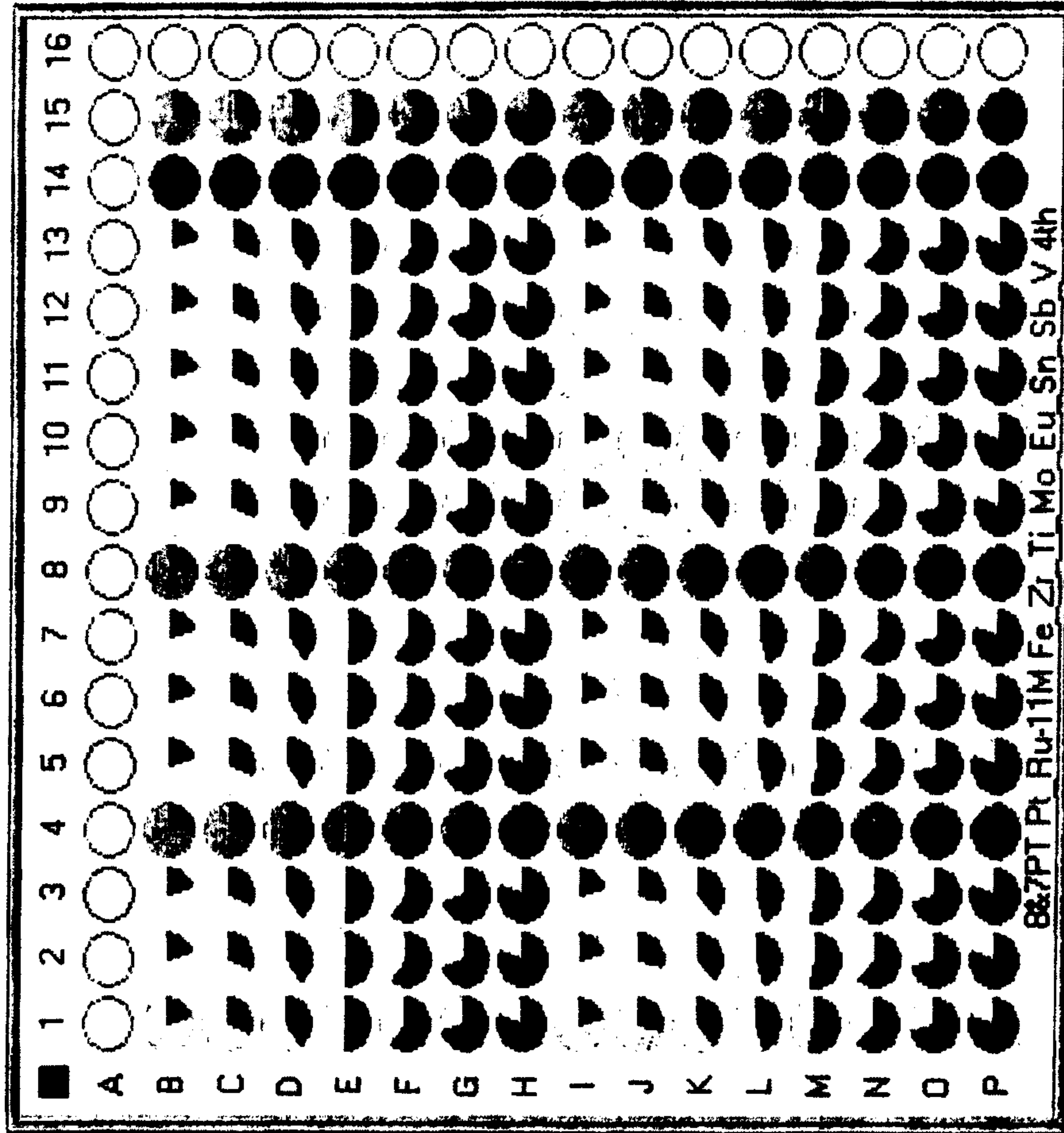


FIG. 3 D

13/43

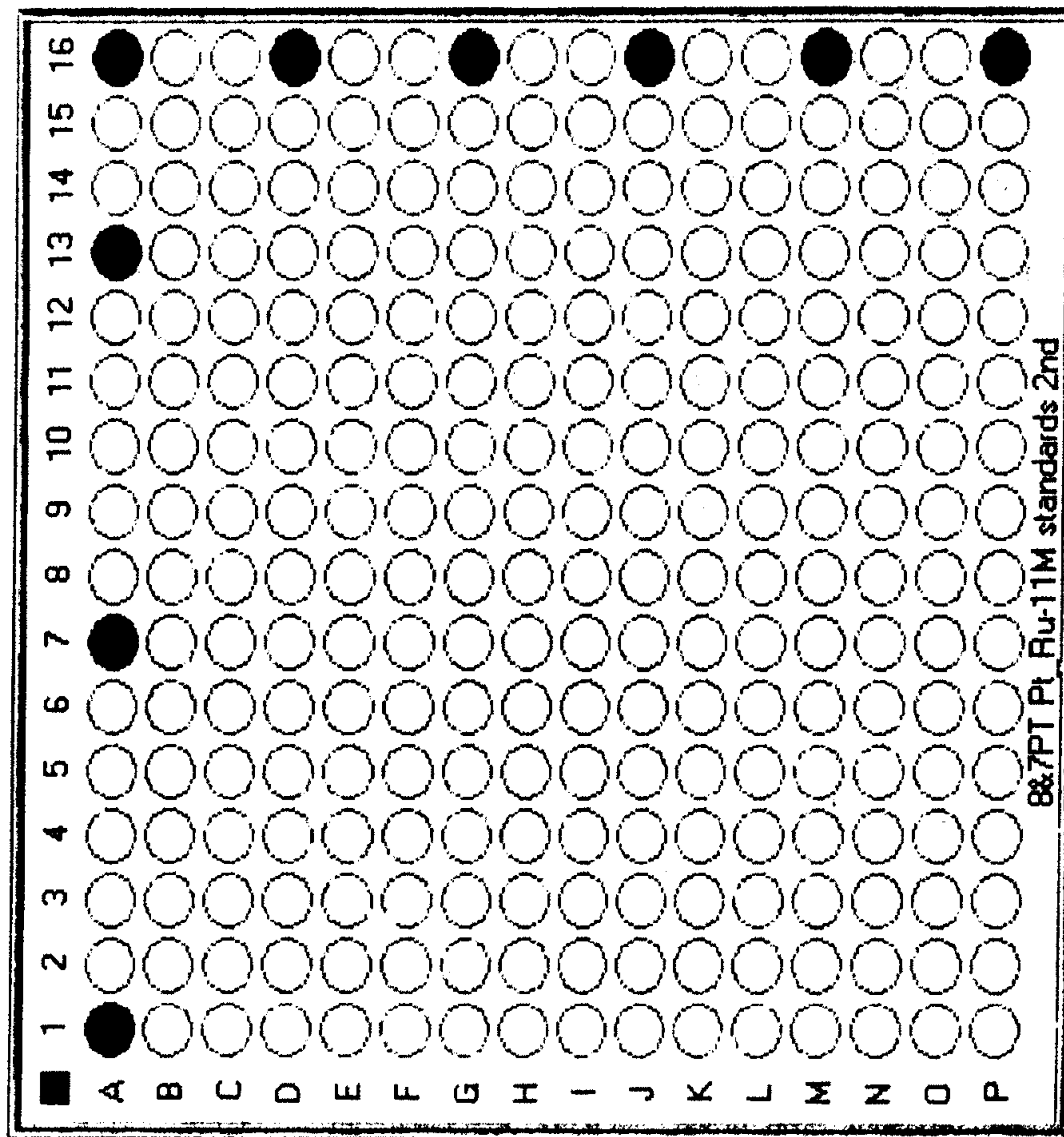


FIG. 3 E

14/43

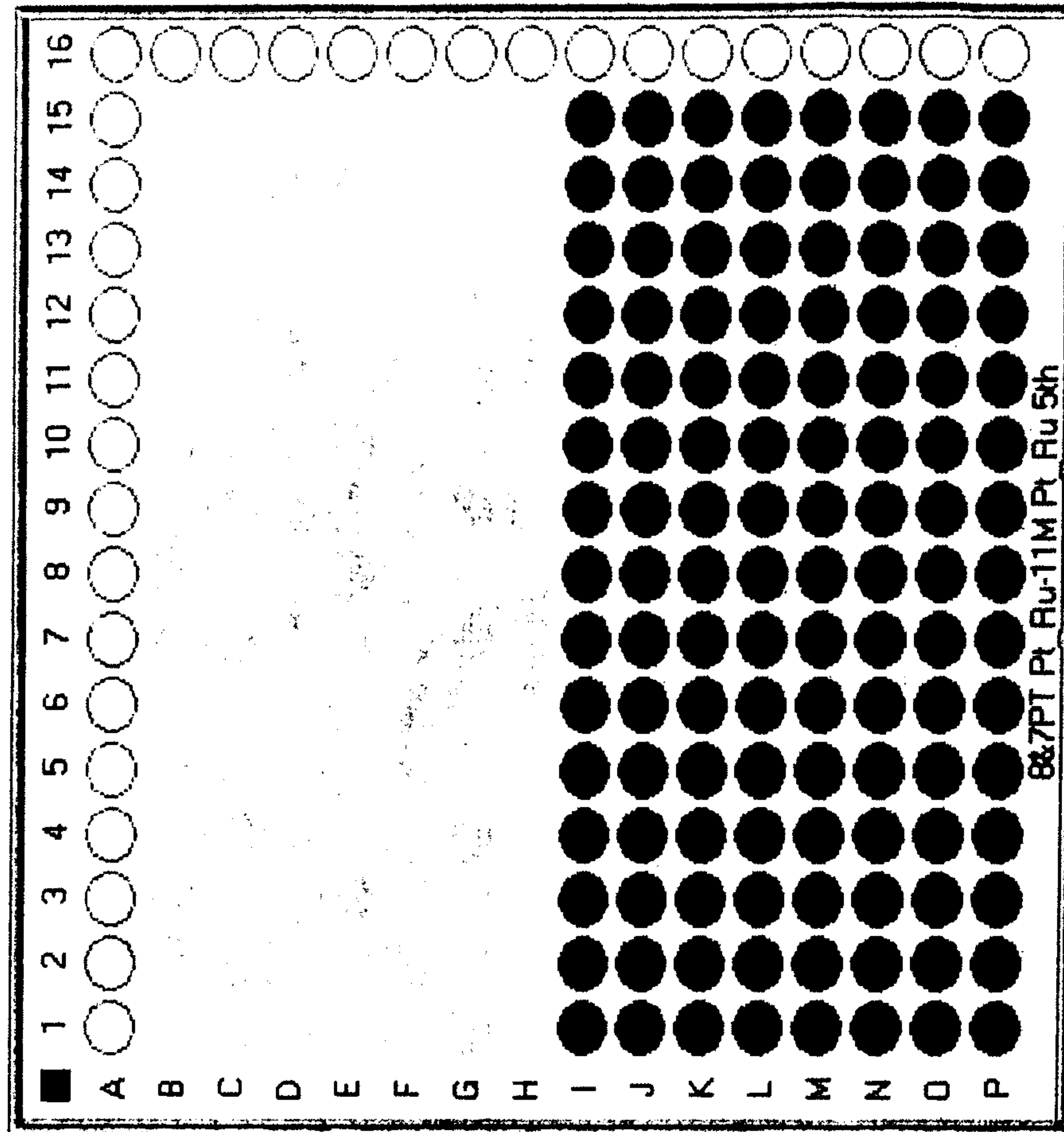


FIG. 3 F

15/43

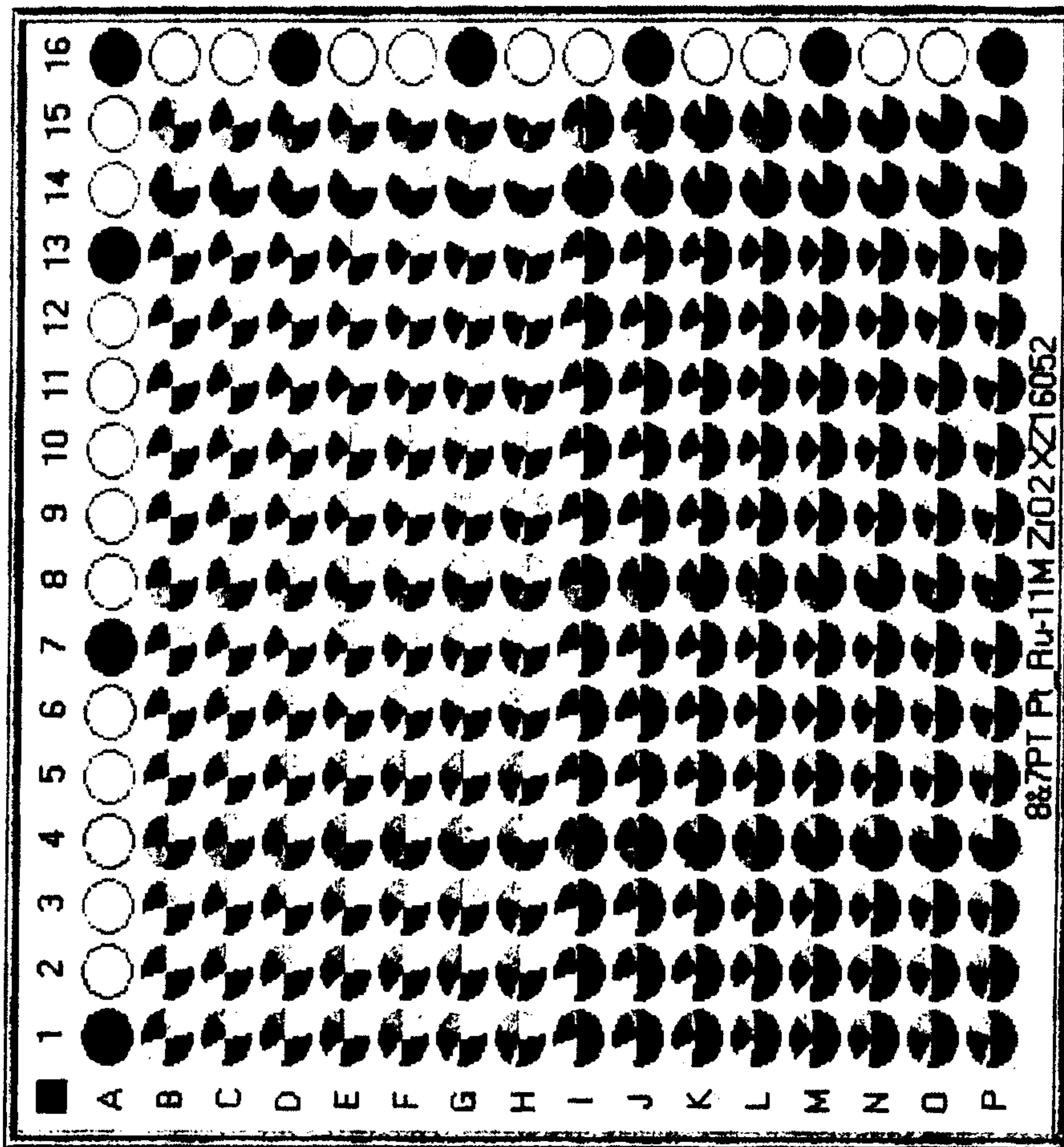
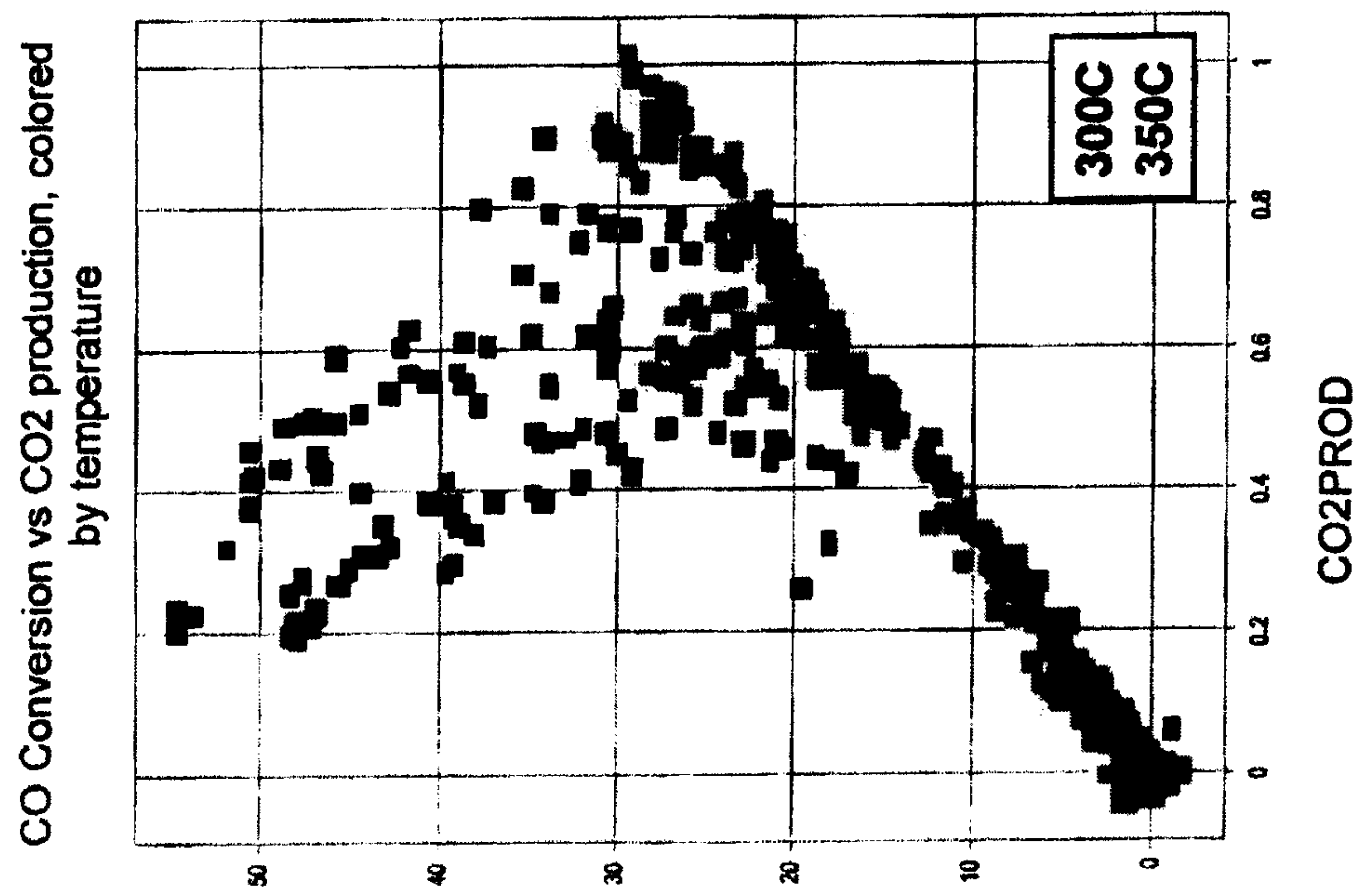


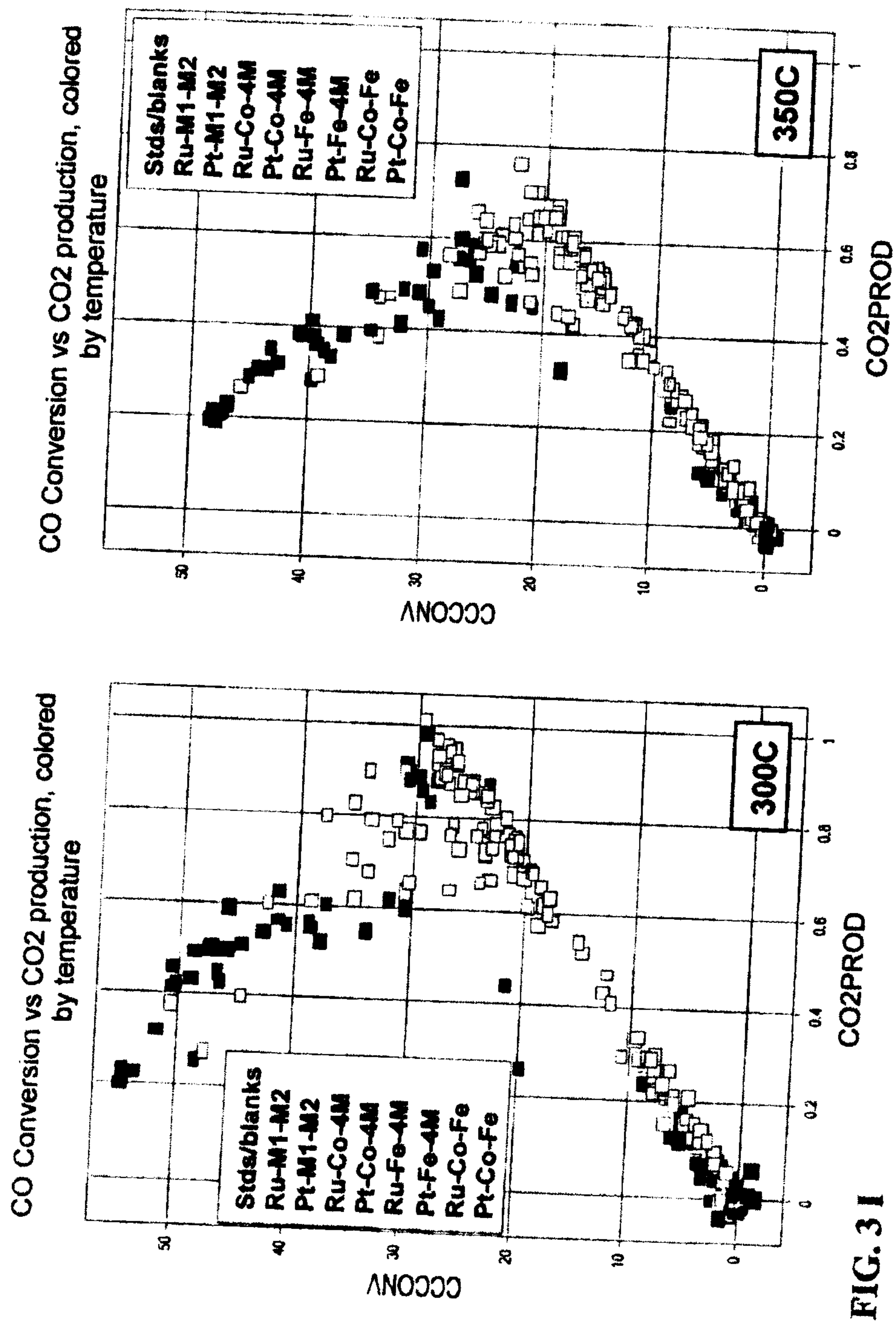
FIG. 3 G

16/43

FIG. 3 H



17/43



18/43

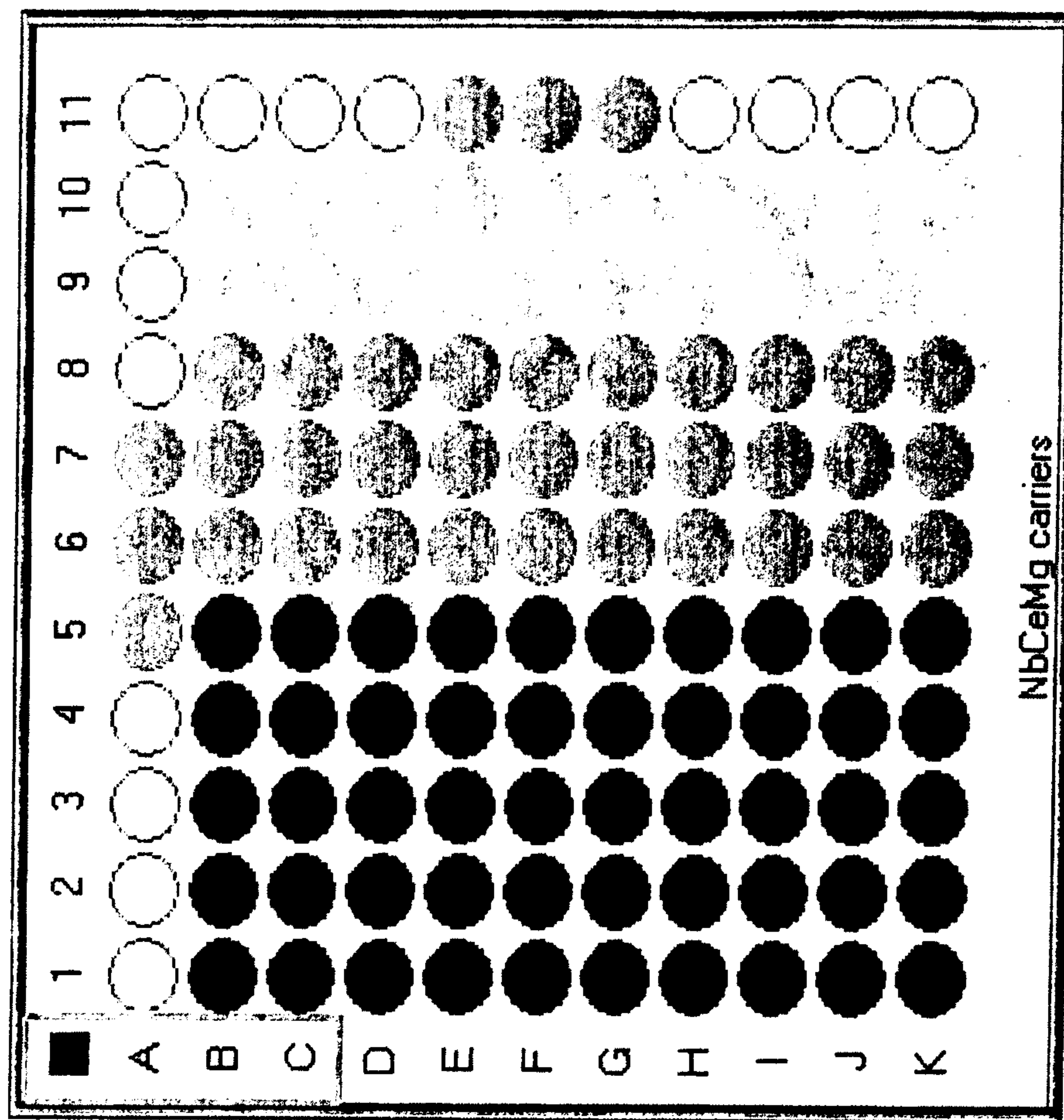


FIG. 4 A

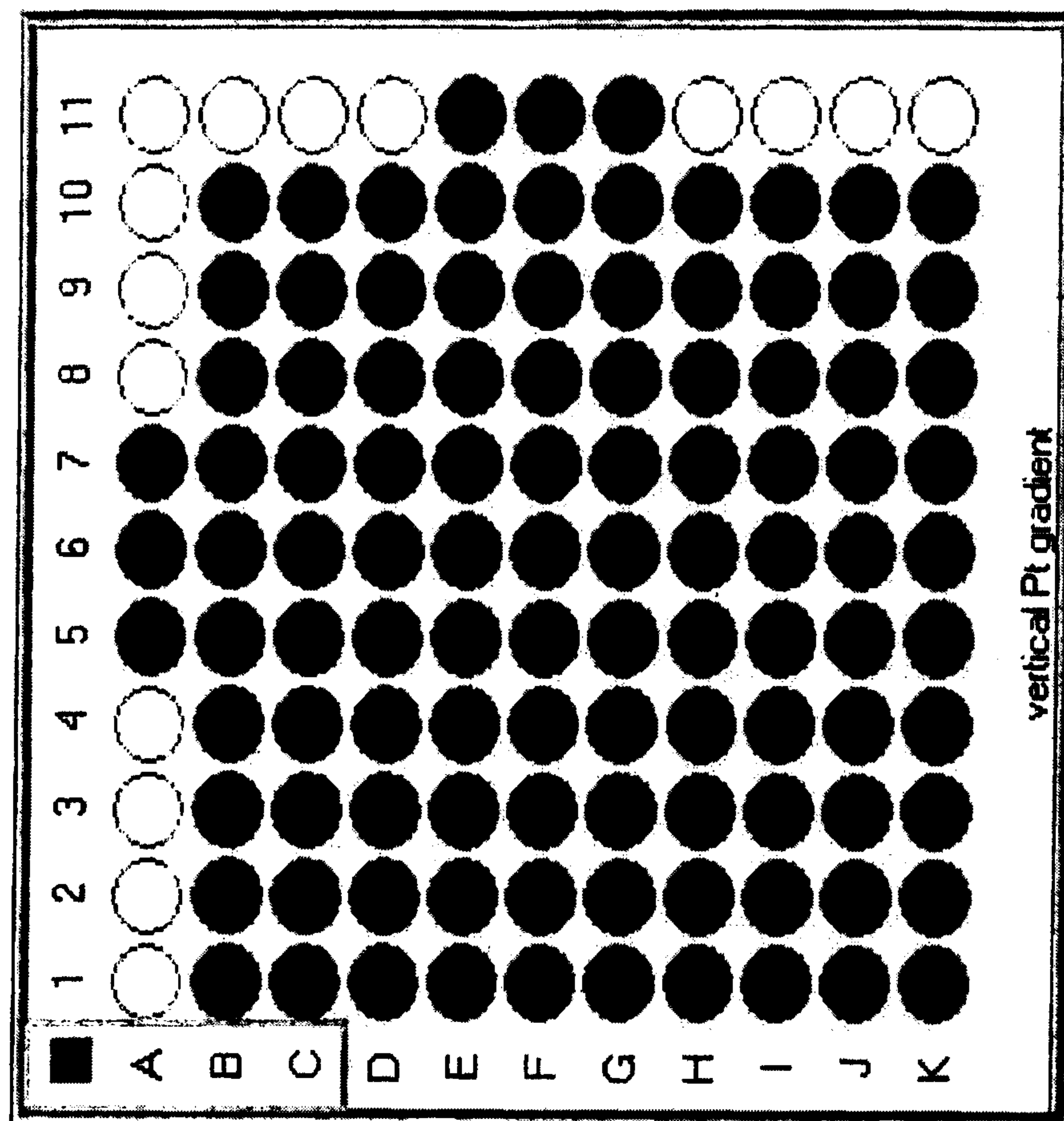


FIG. 4 B

Legend:

-  $\text{Pt}(\text{NH}_3)_2\text{NO}_2$ 5% Pt
-  $\text{H}_2\text{O-s}$

20/43

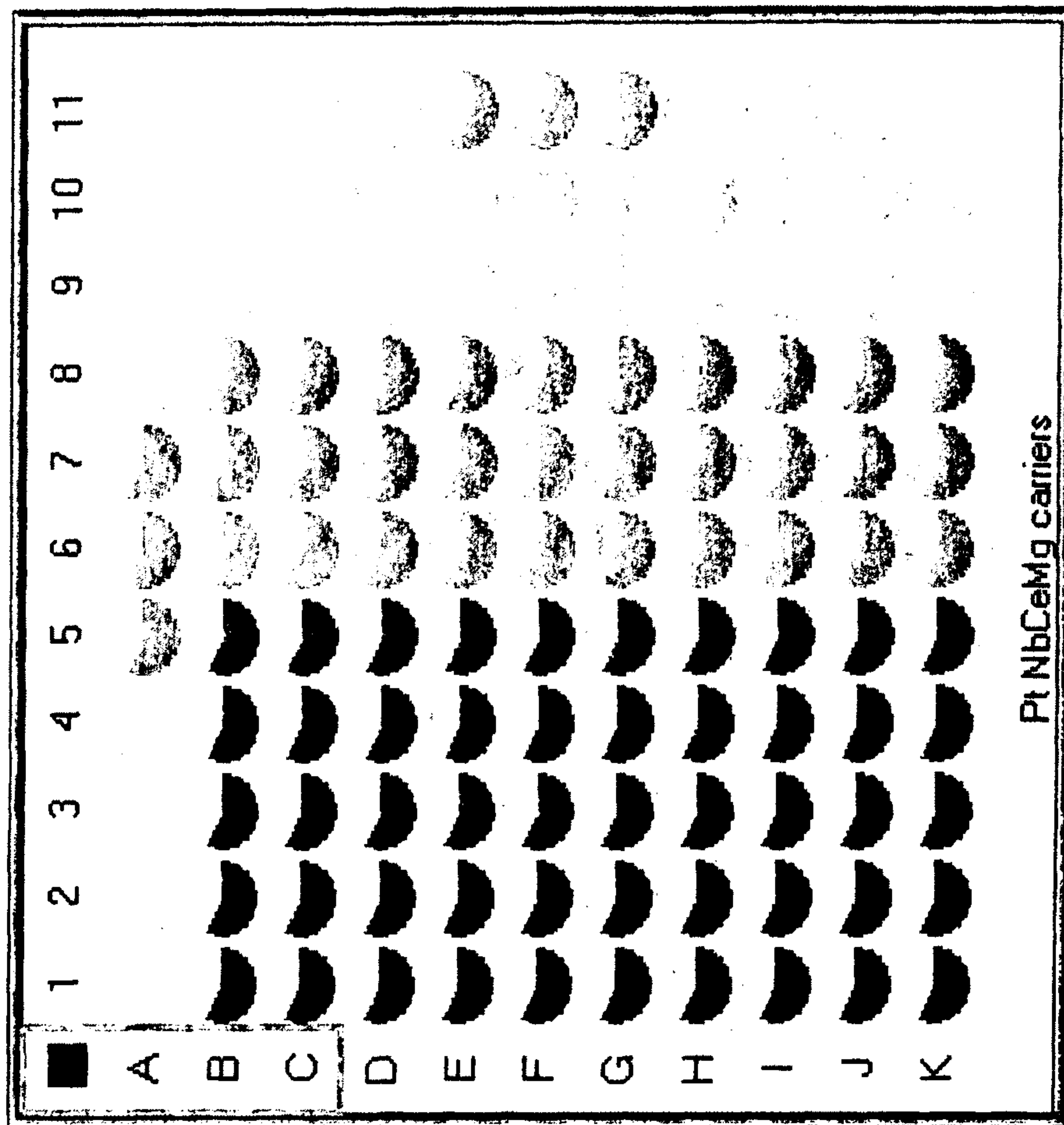
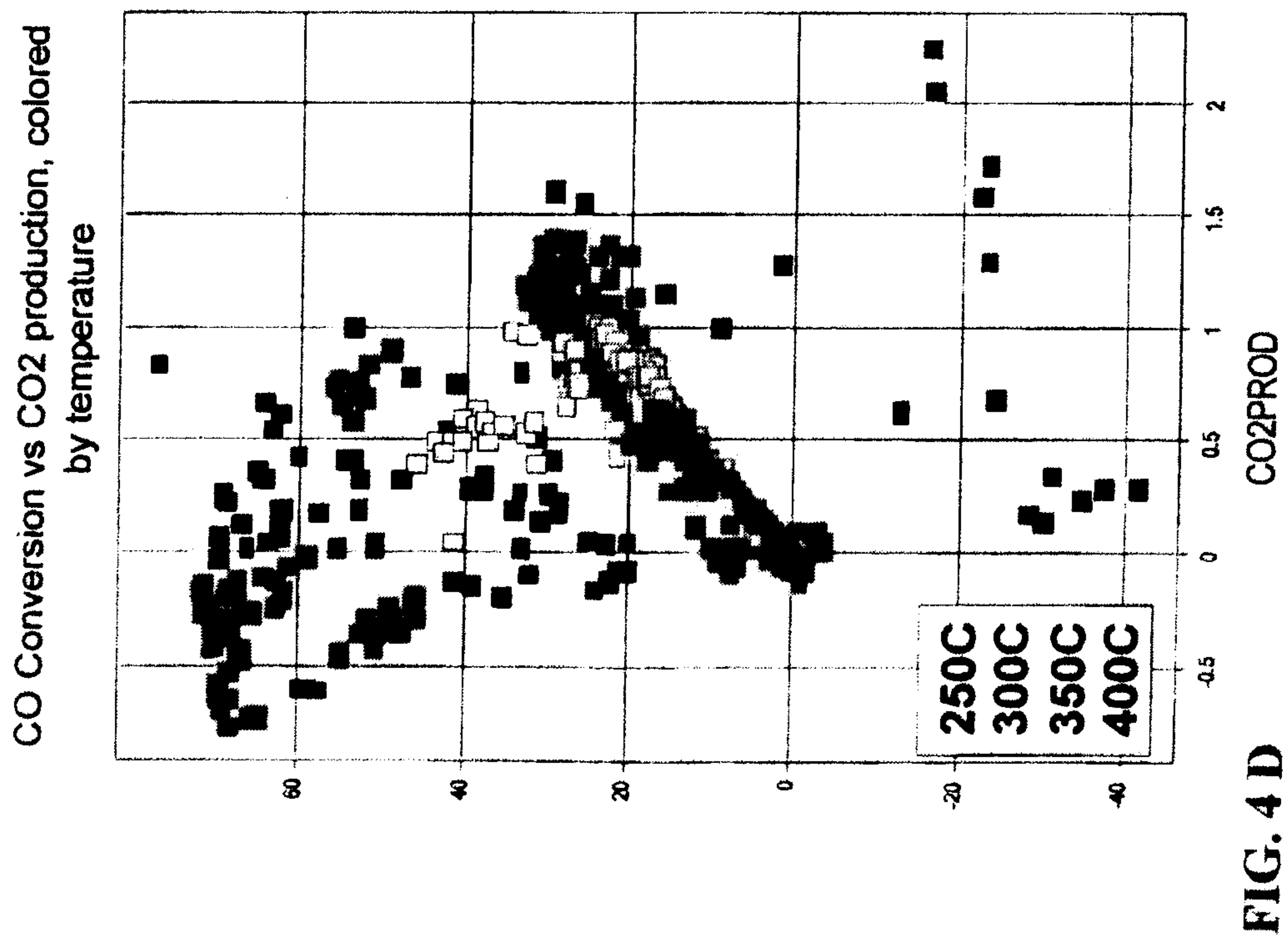
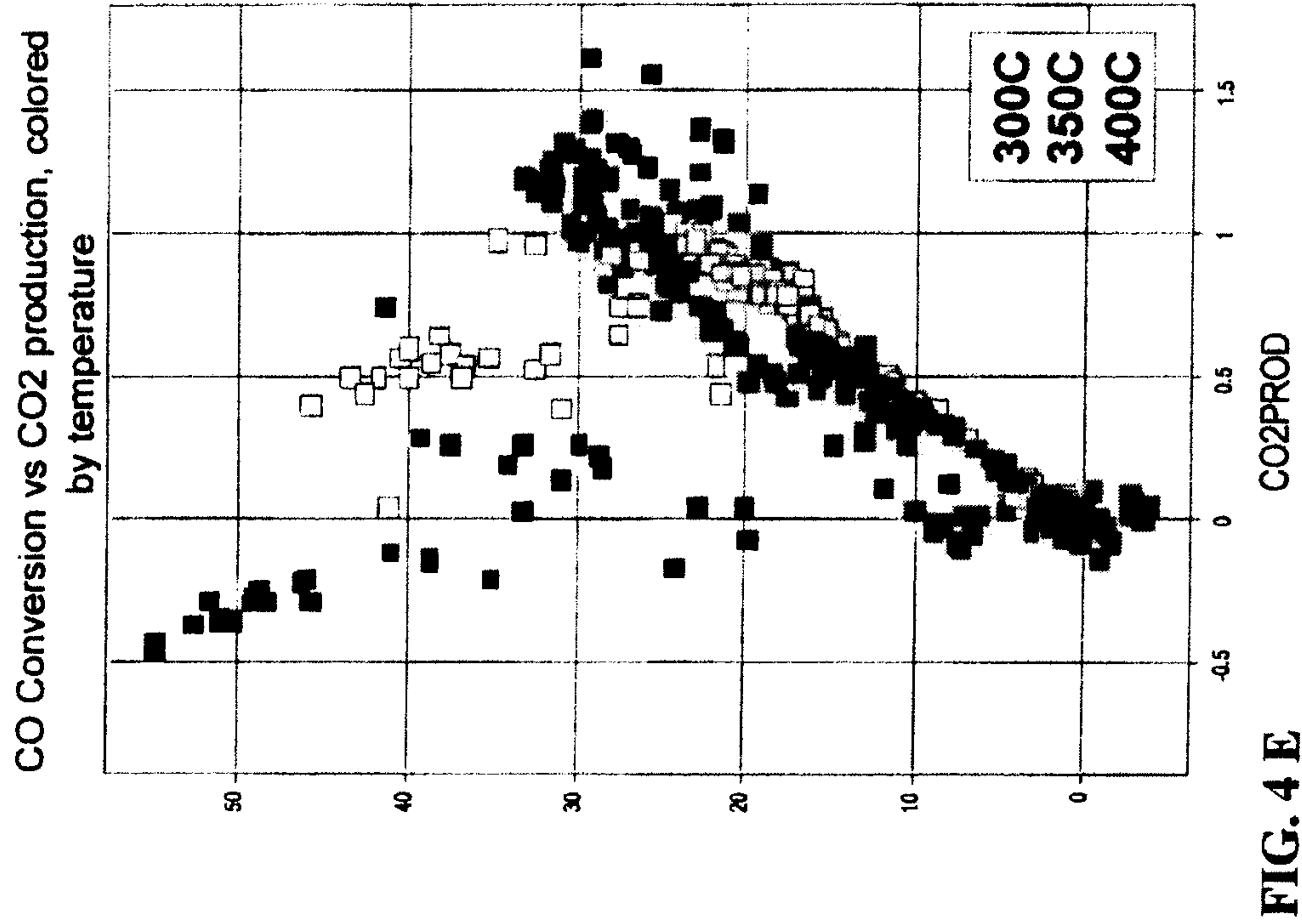
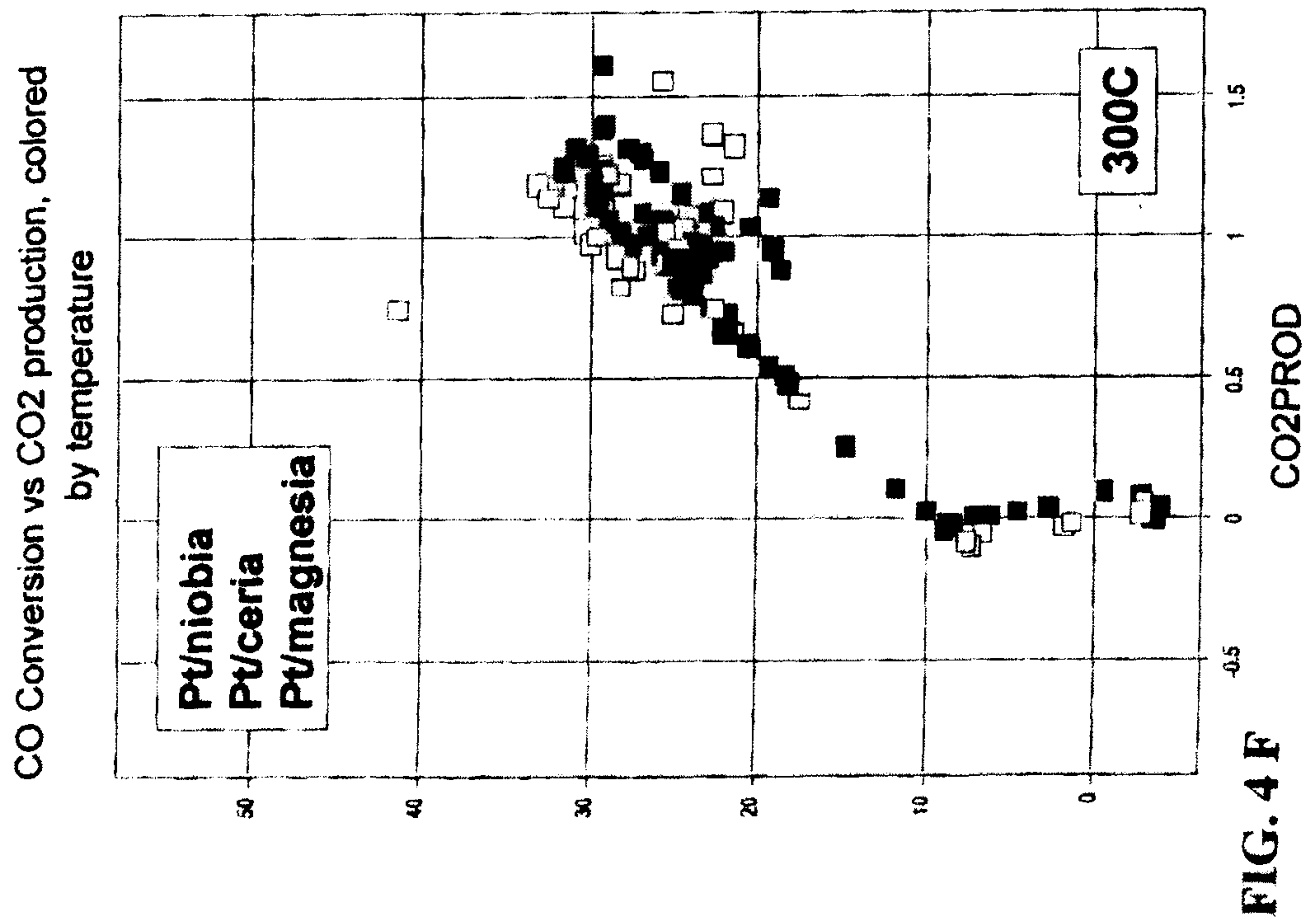
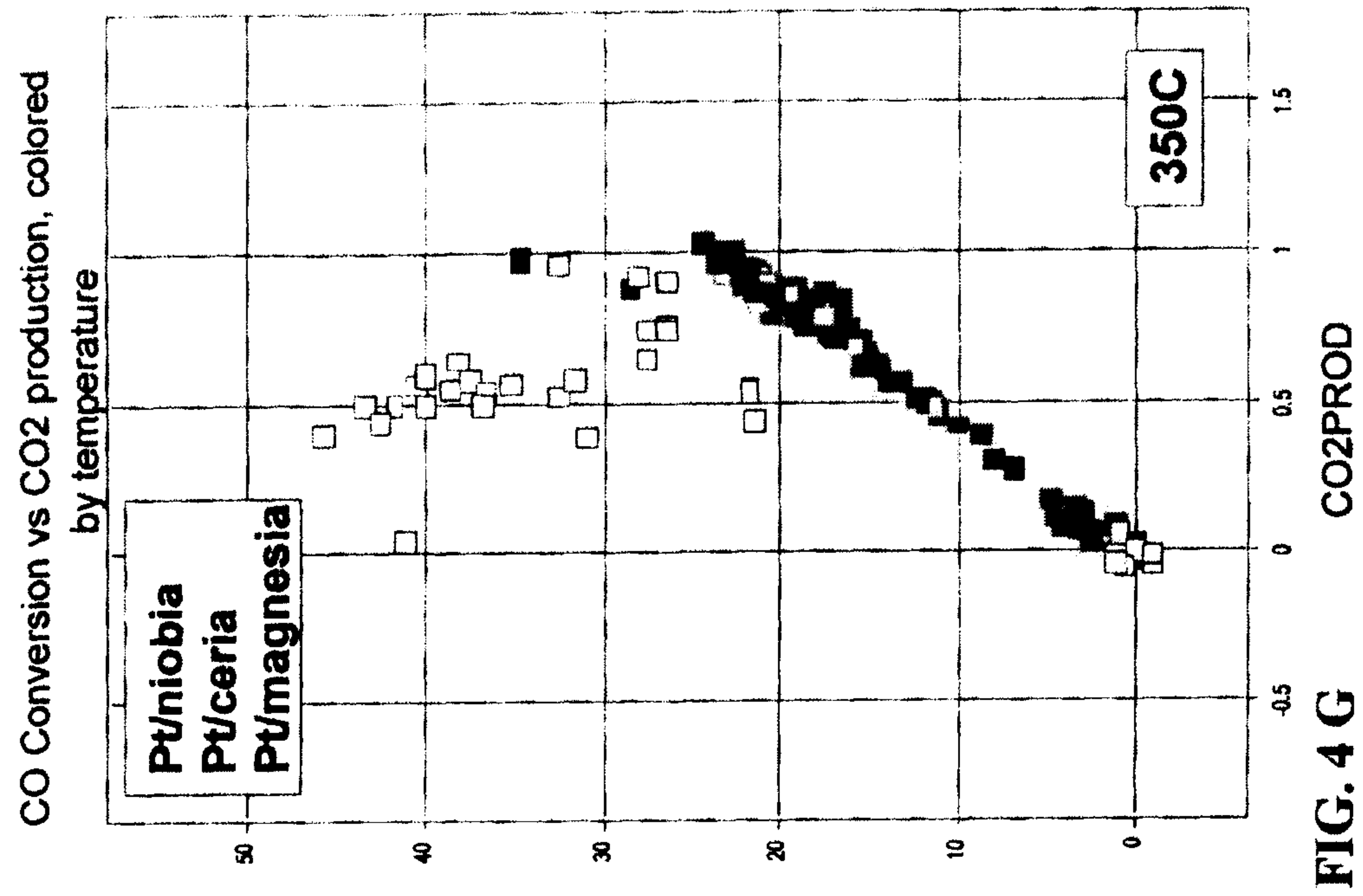


FIG. 4 C

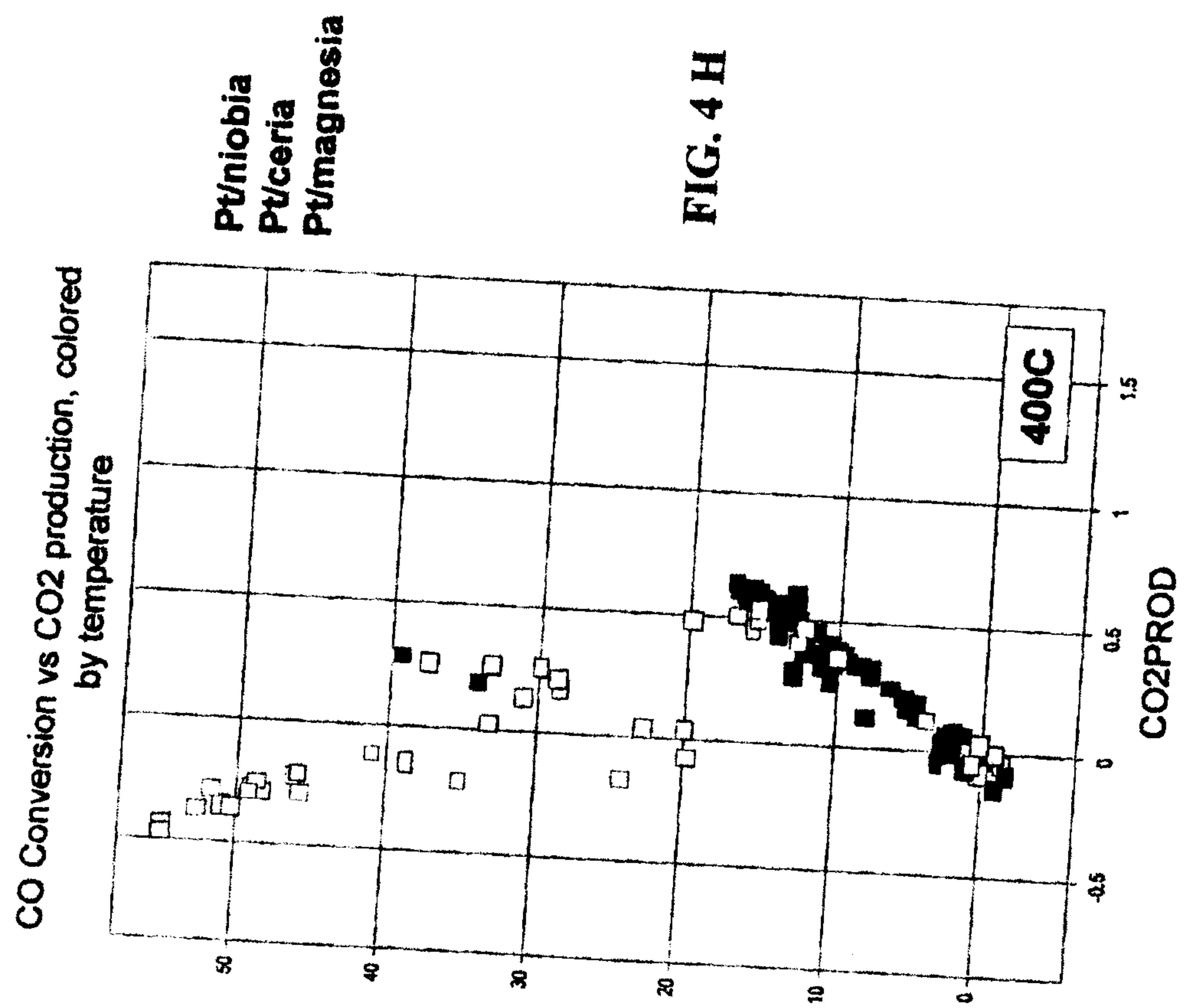
21/43



22/43



23/43



24/43

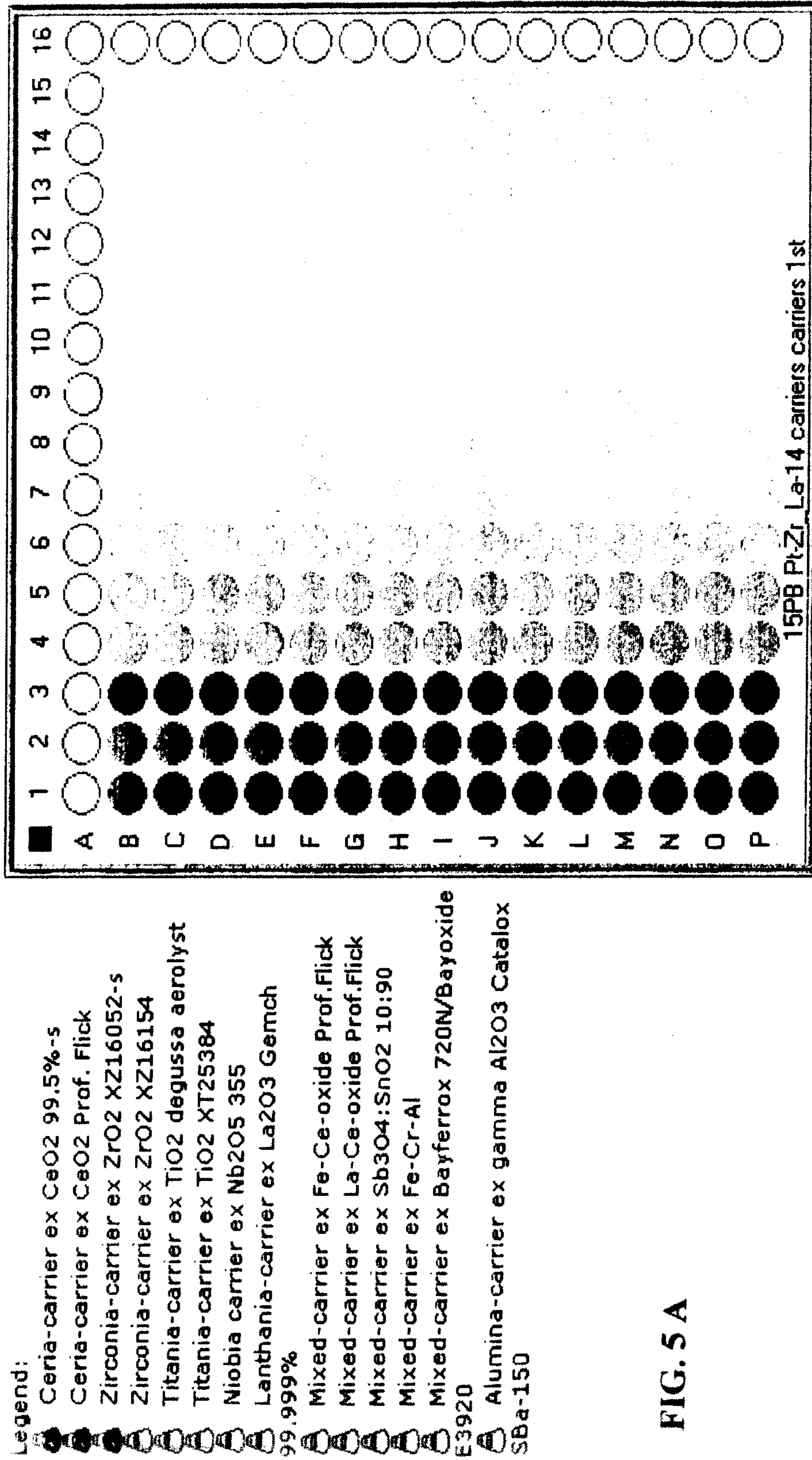


FIG. 5 A

25/43

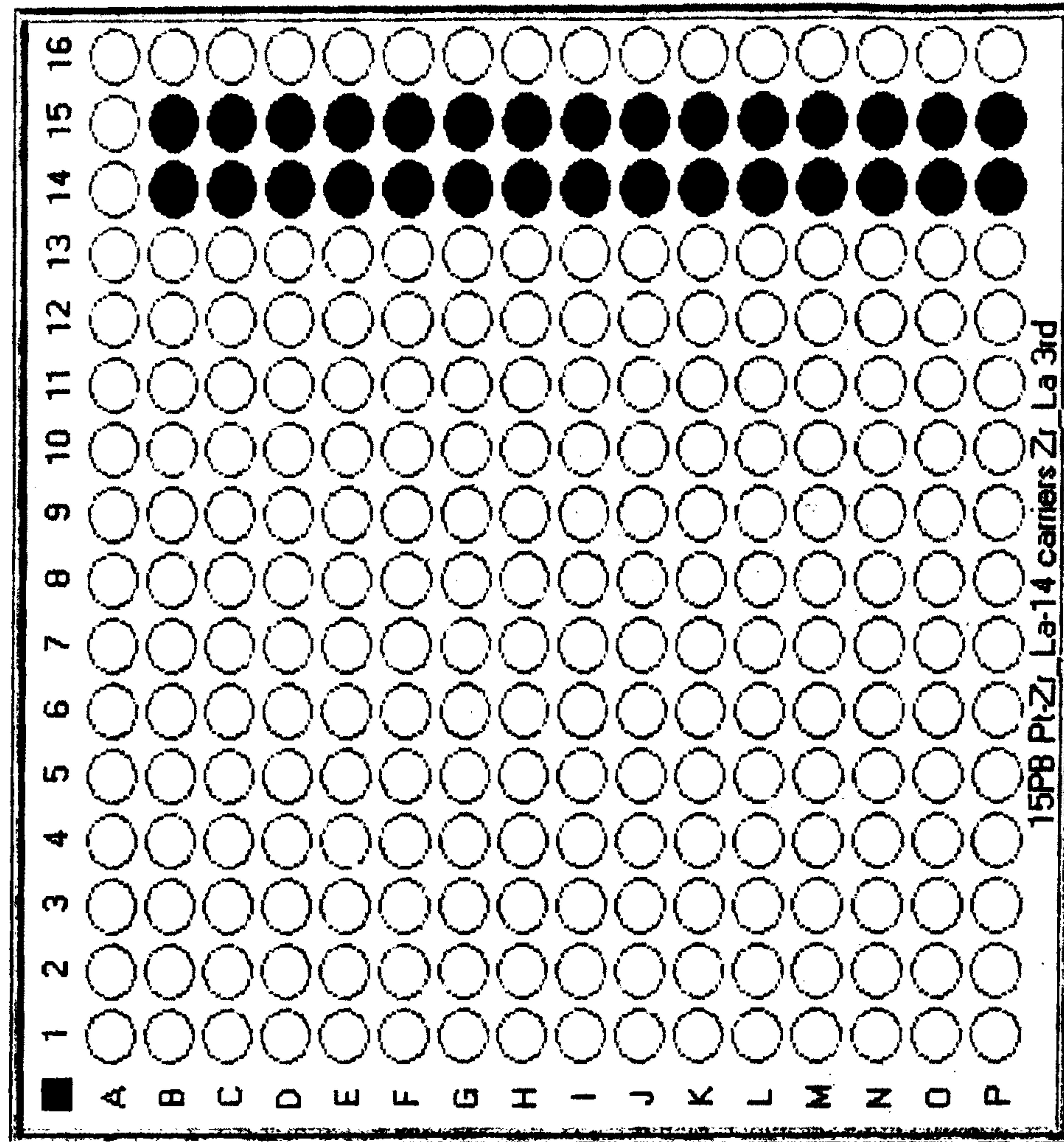
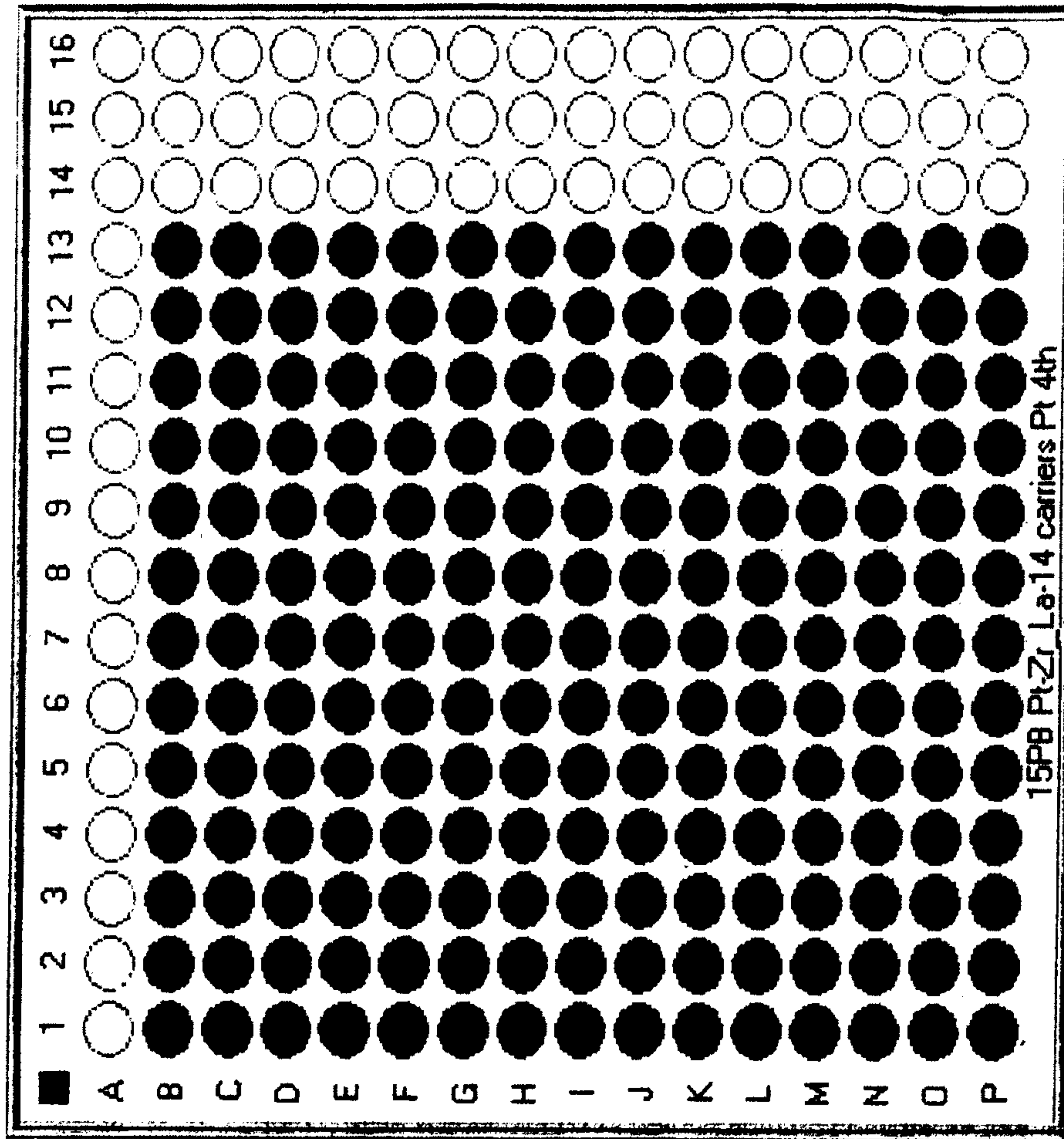


FIG. 5 B

26/43



Legend:

● Platinum ex PtNH₃2NO₂2 (unstabilized)

○ 1%Pt

● H₂O

FIG. 5 C

27/43

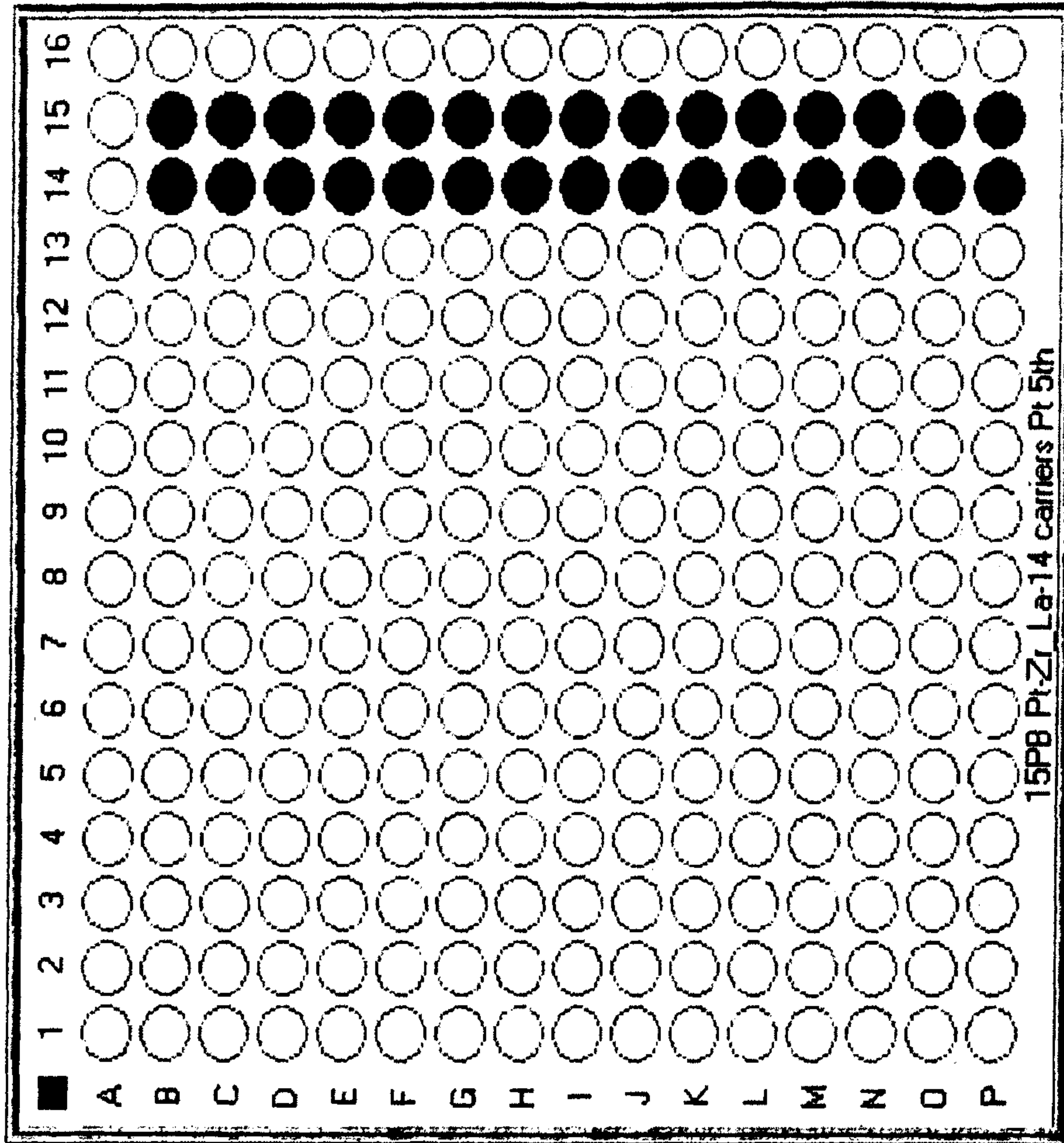


FIG. 5 D

28/43

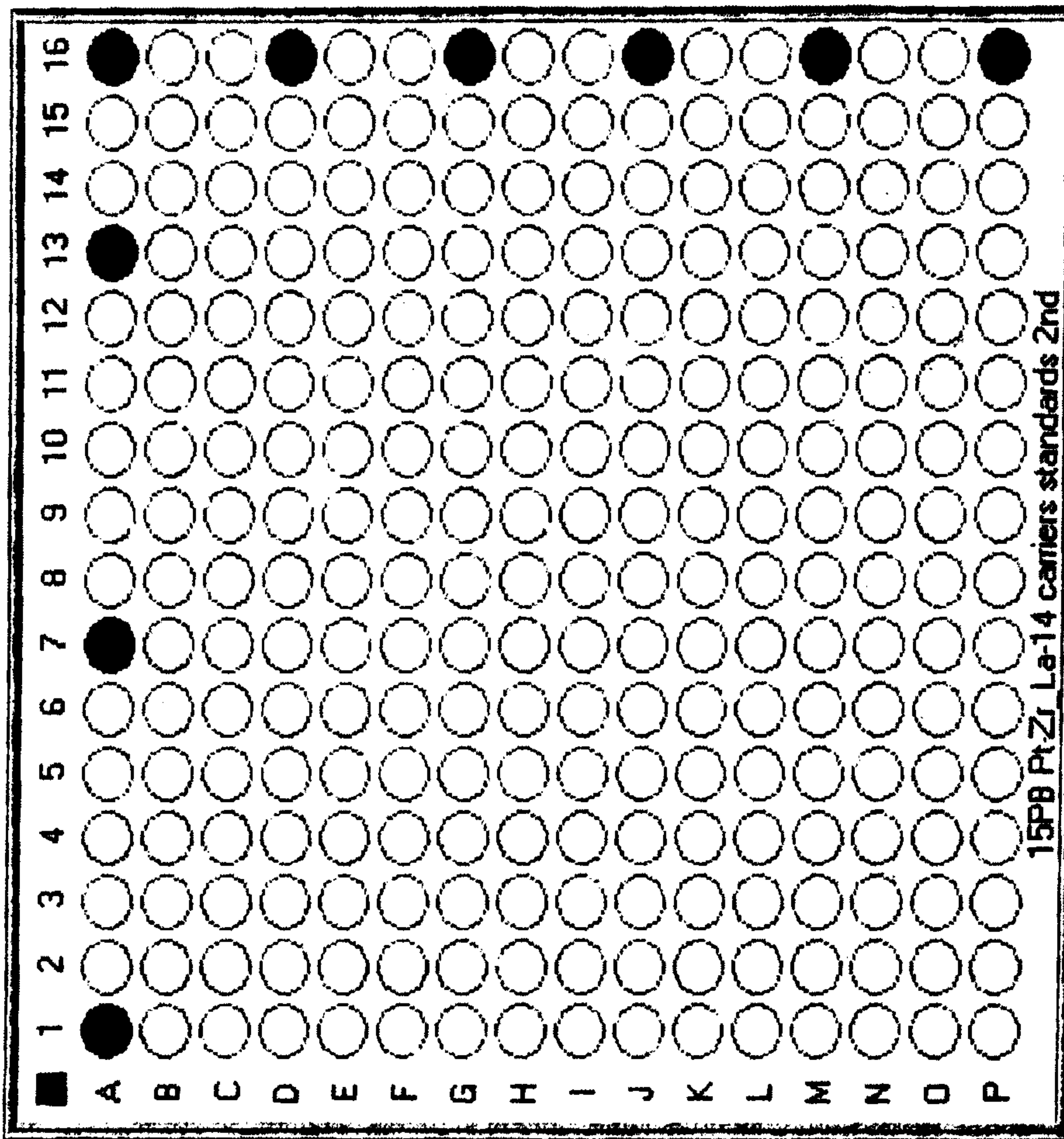


FIG. 5 E

29/43

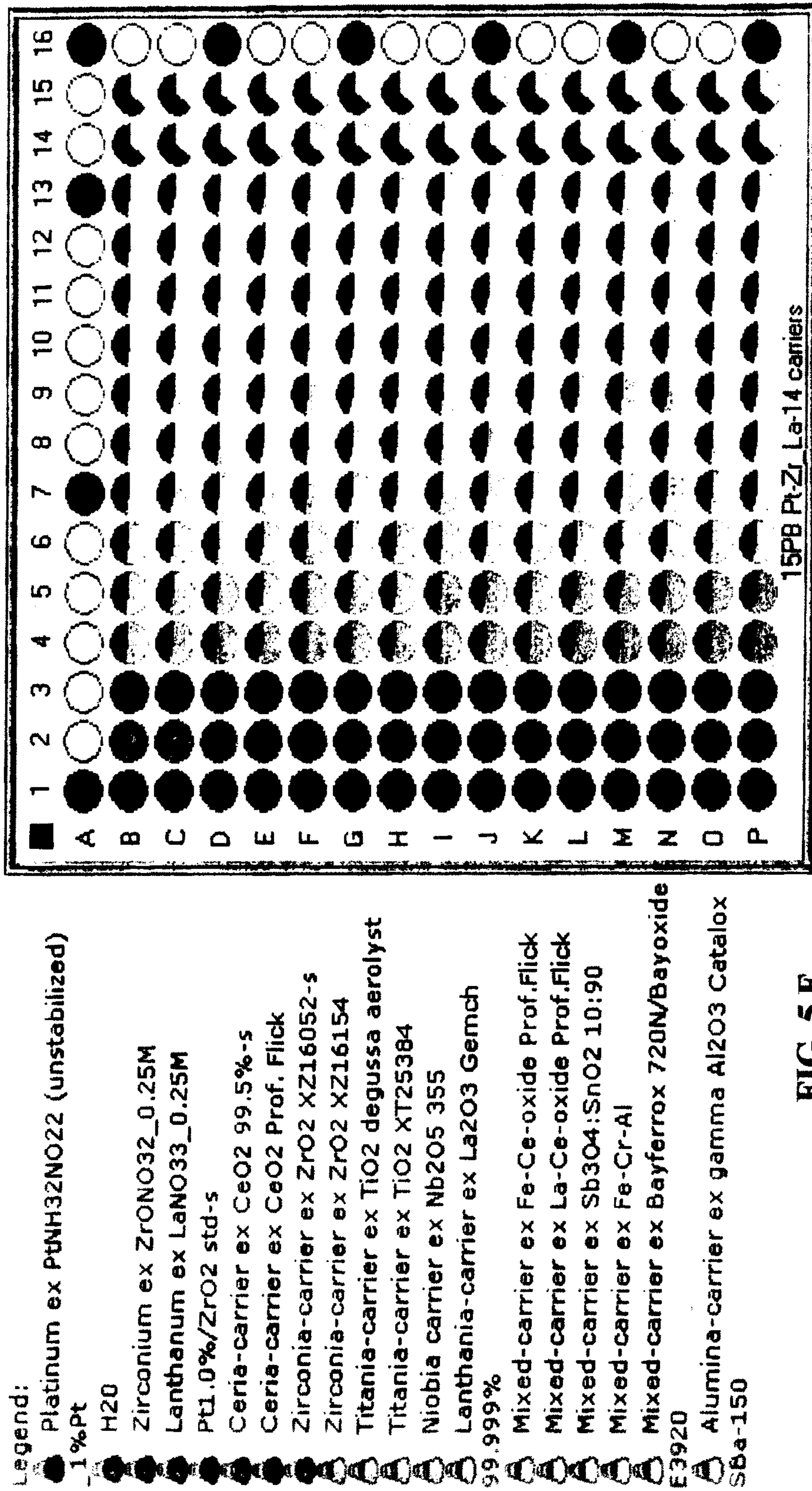
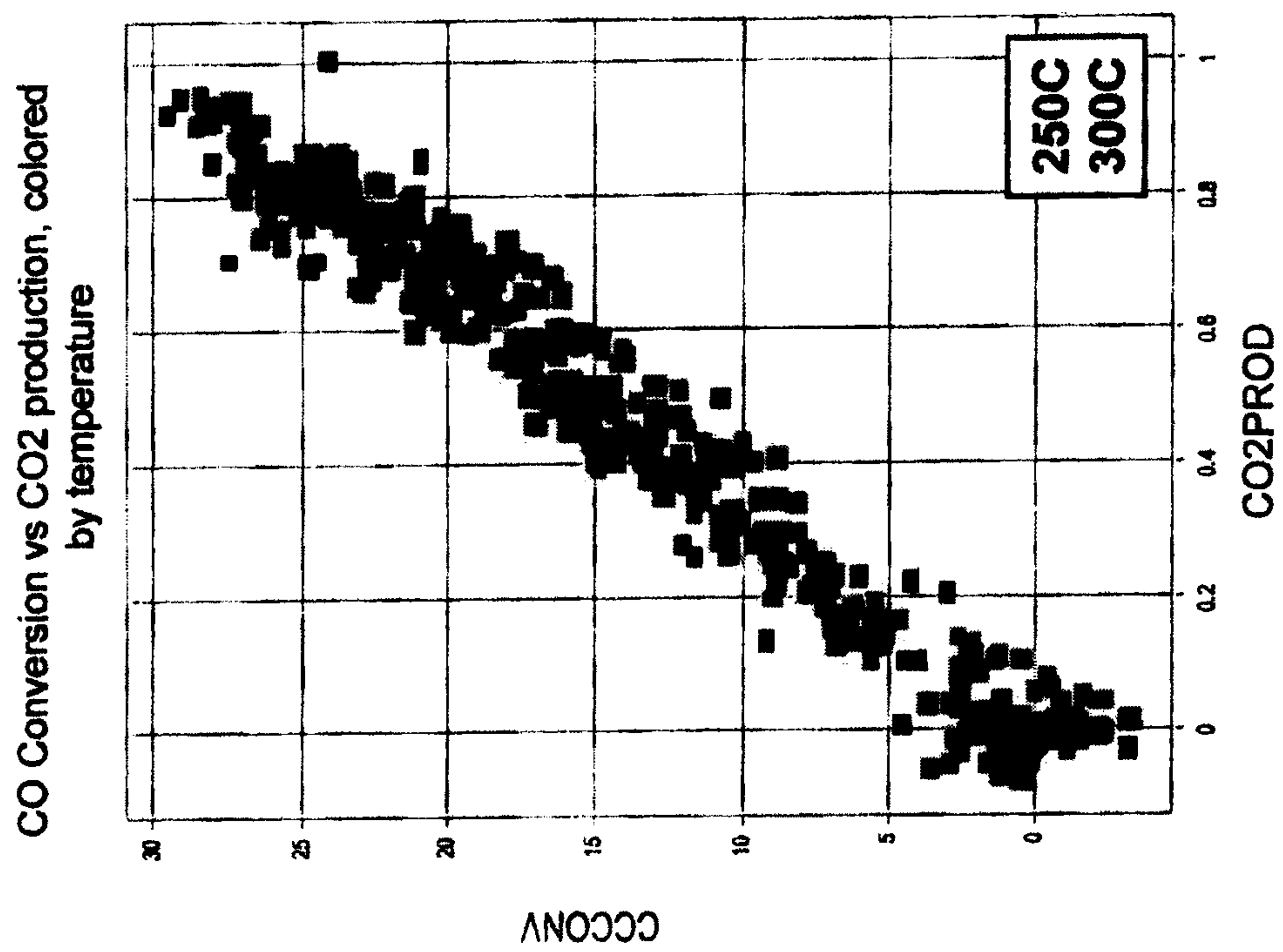


FIG. 5 F

30/43

FIG. 5 G



31/43

CO Conversion vs CO2 production, colored
by temperature

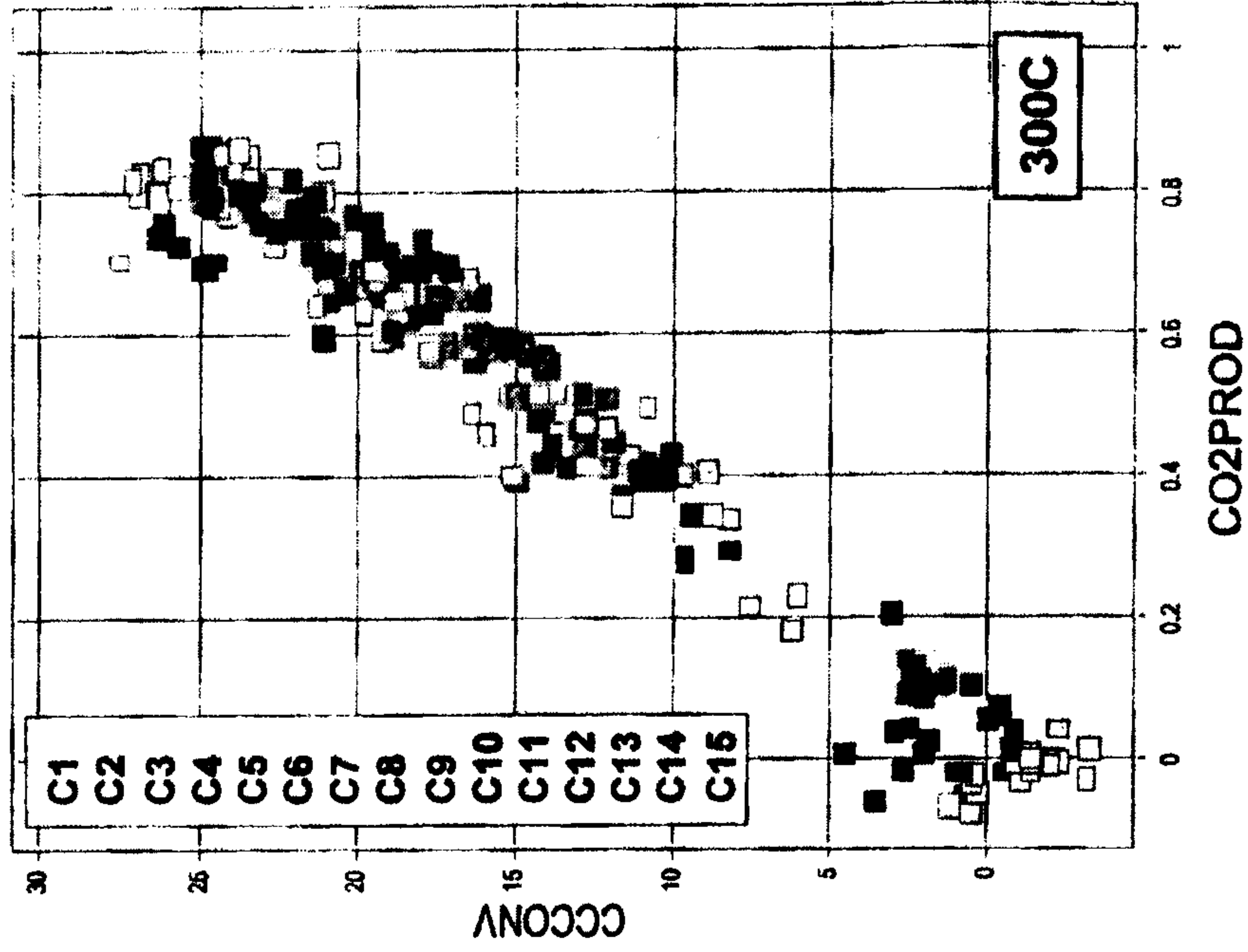


FIG. 5 I

CO Conversion vs CO2 production, colored
by temperature

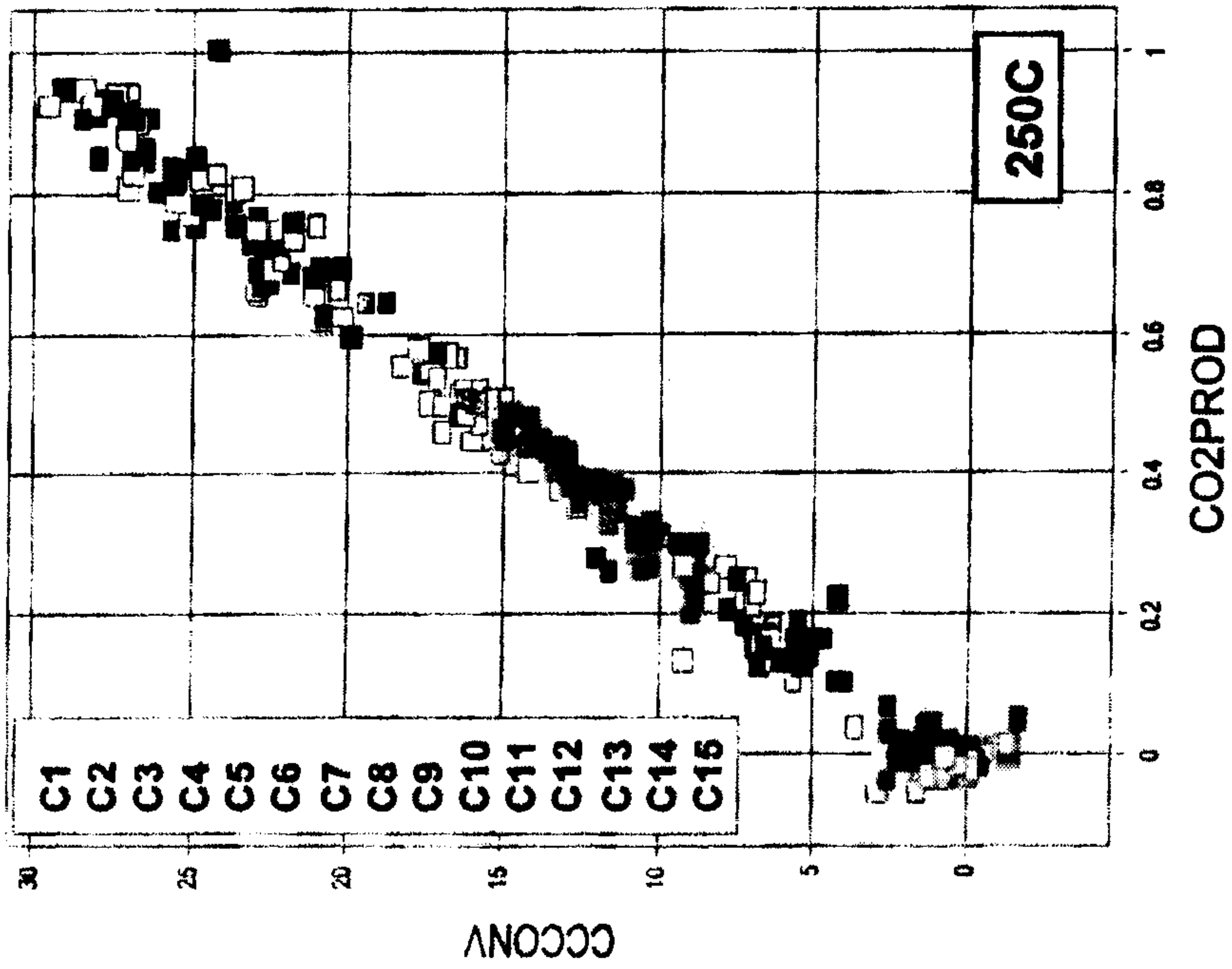


FIG. 5 H

32/43

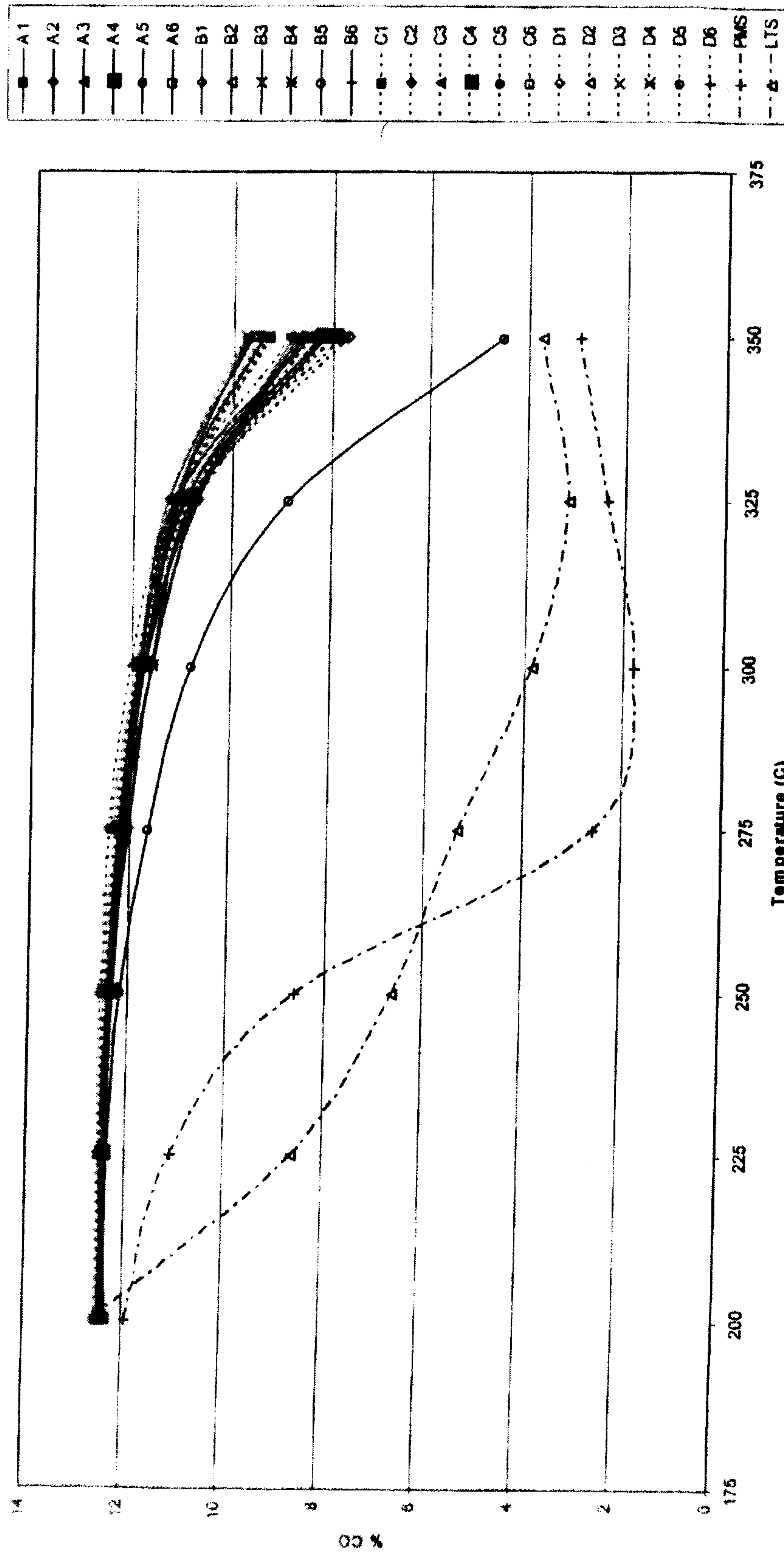


FIG. 6

33/43

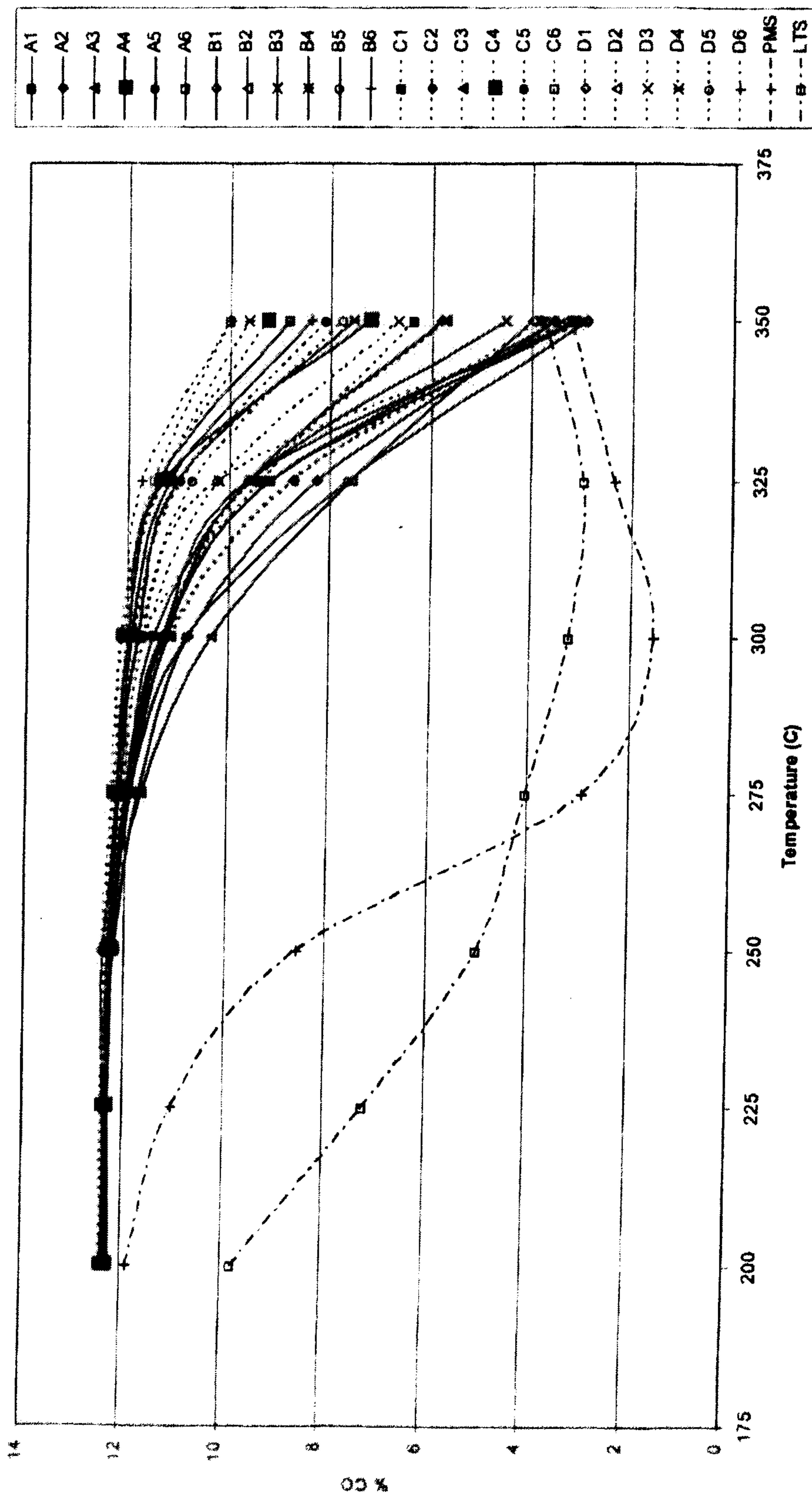


FIG. 7

34/43

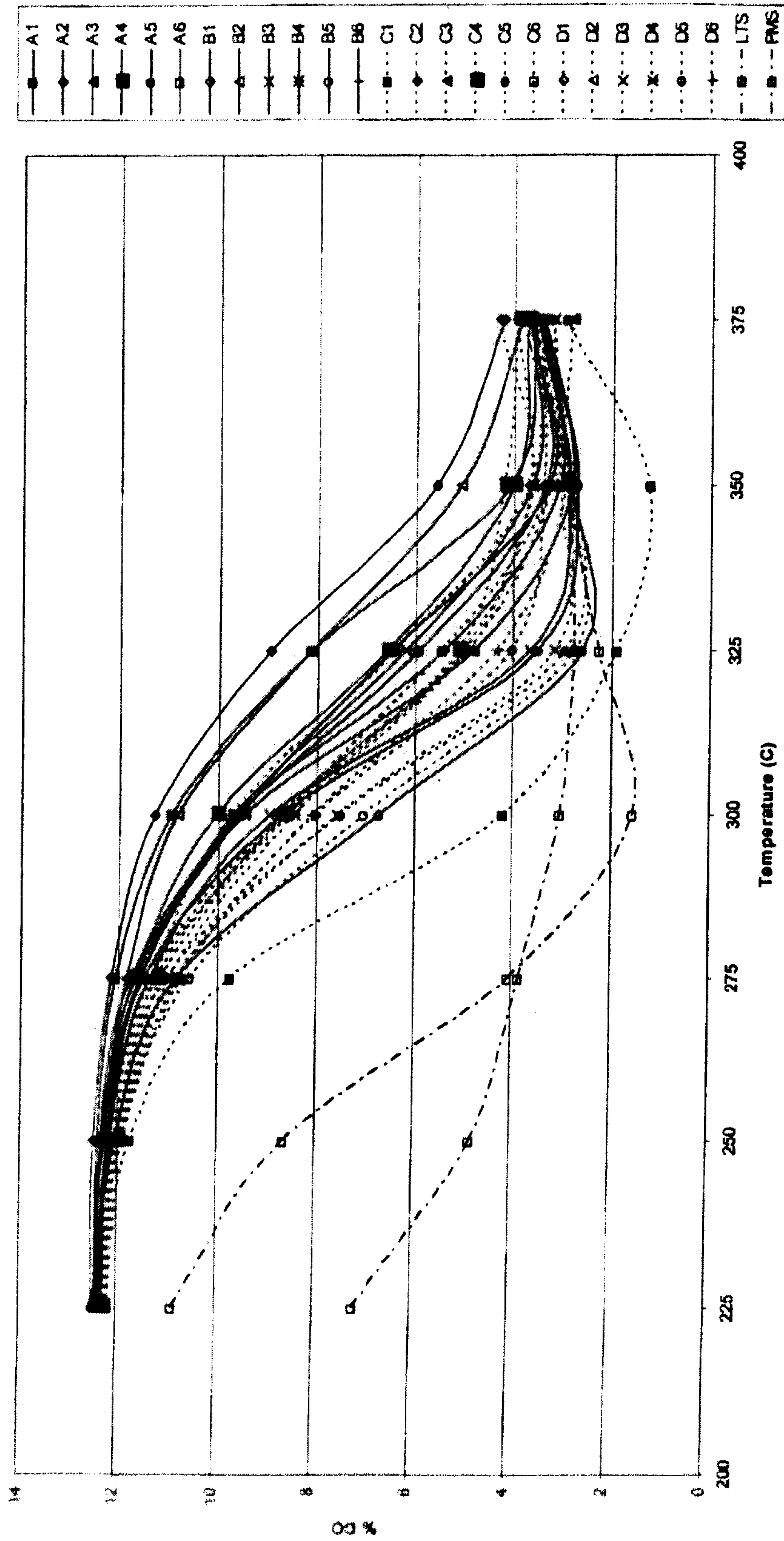


FIG. 8

35/43

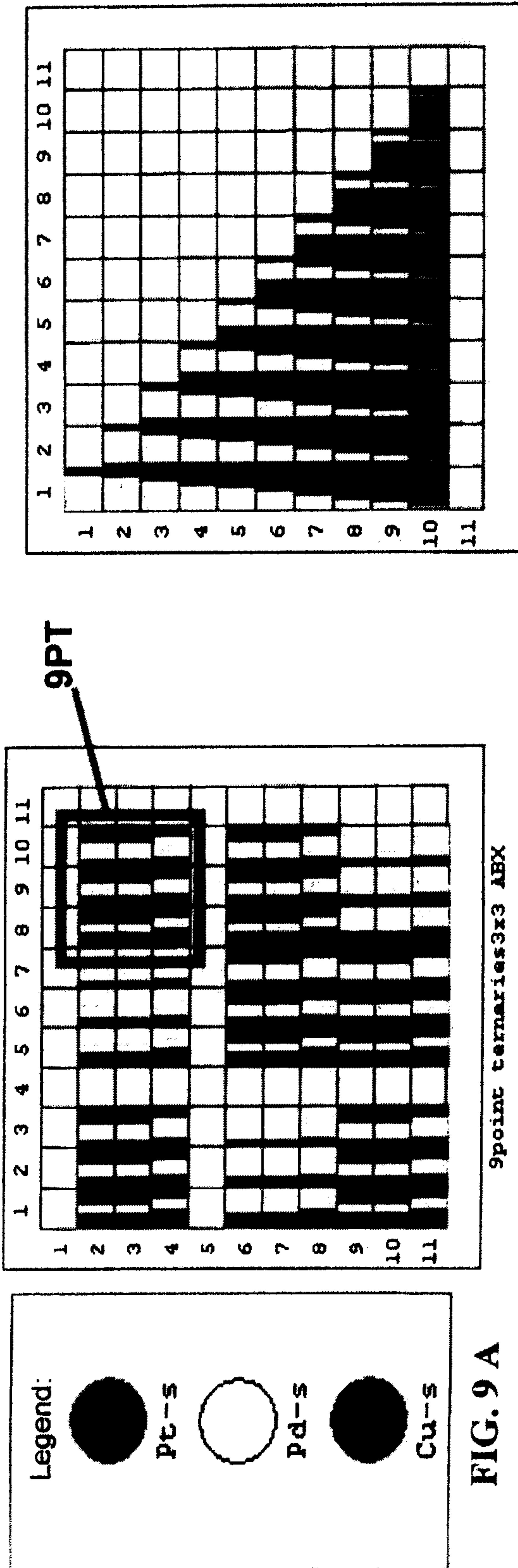


FIG. 9 C

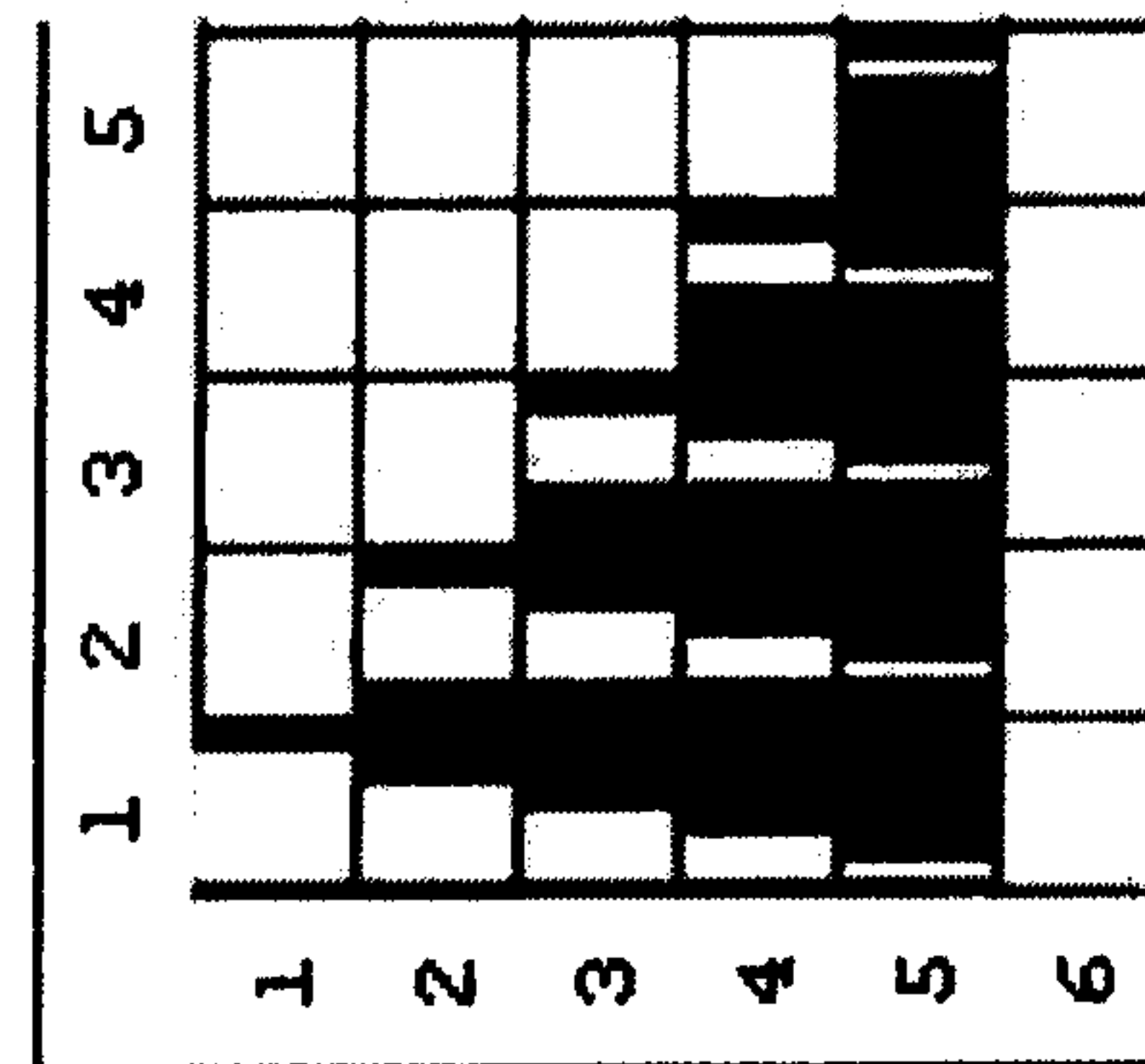


FIG. 9 B

36/43

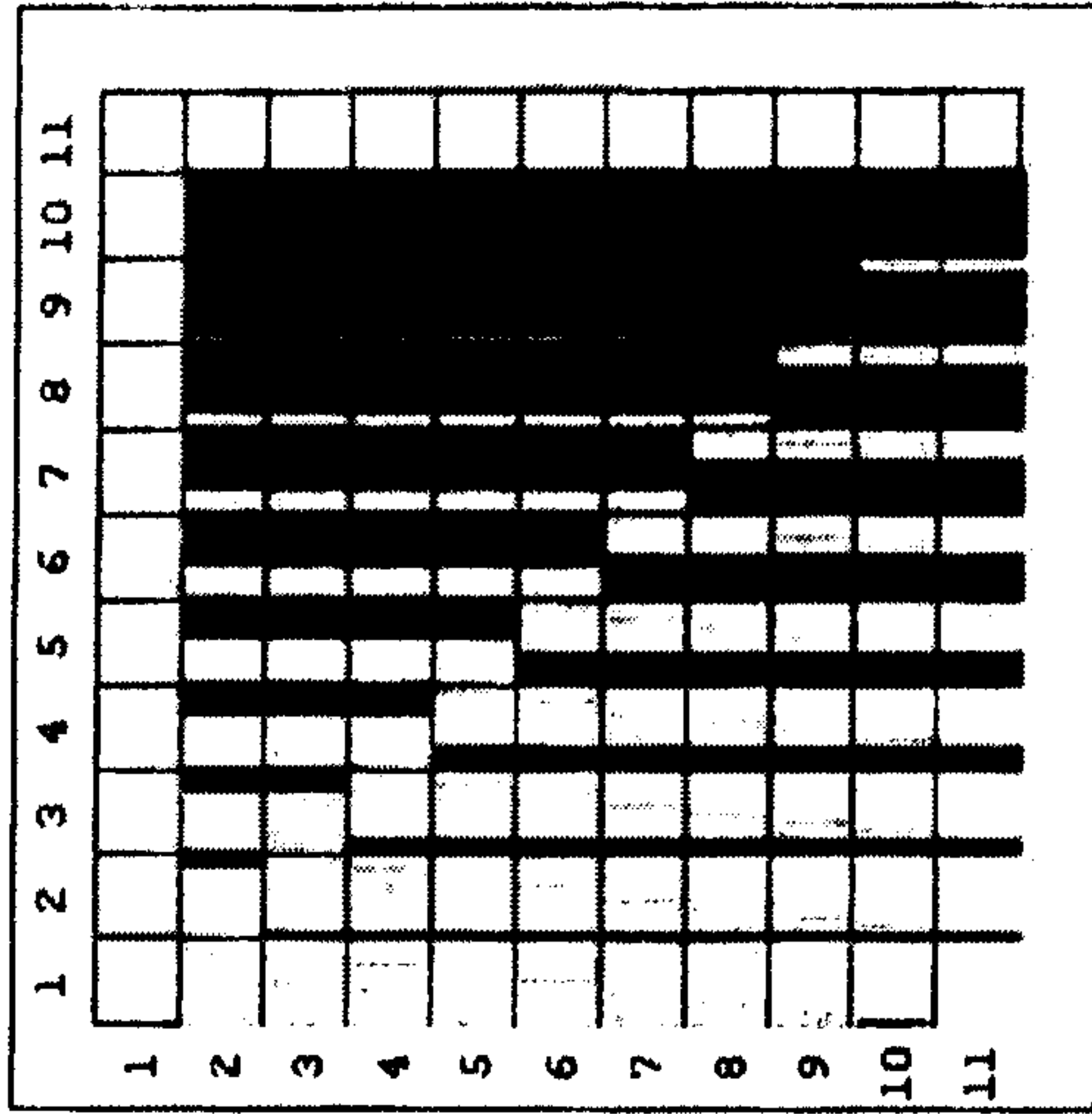
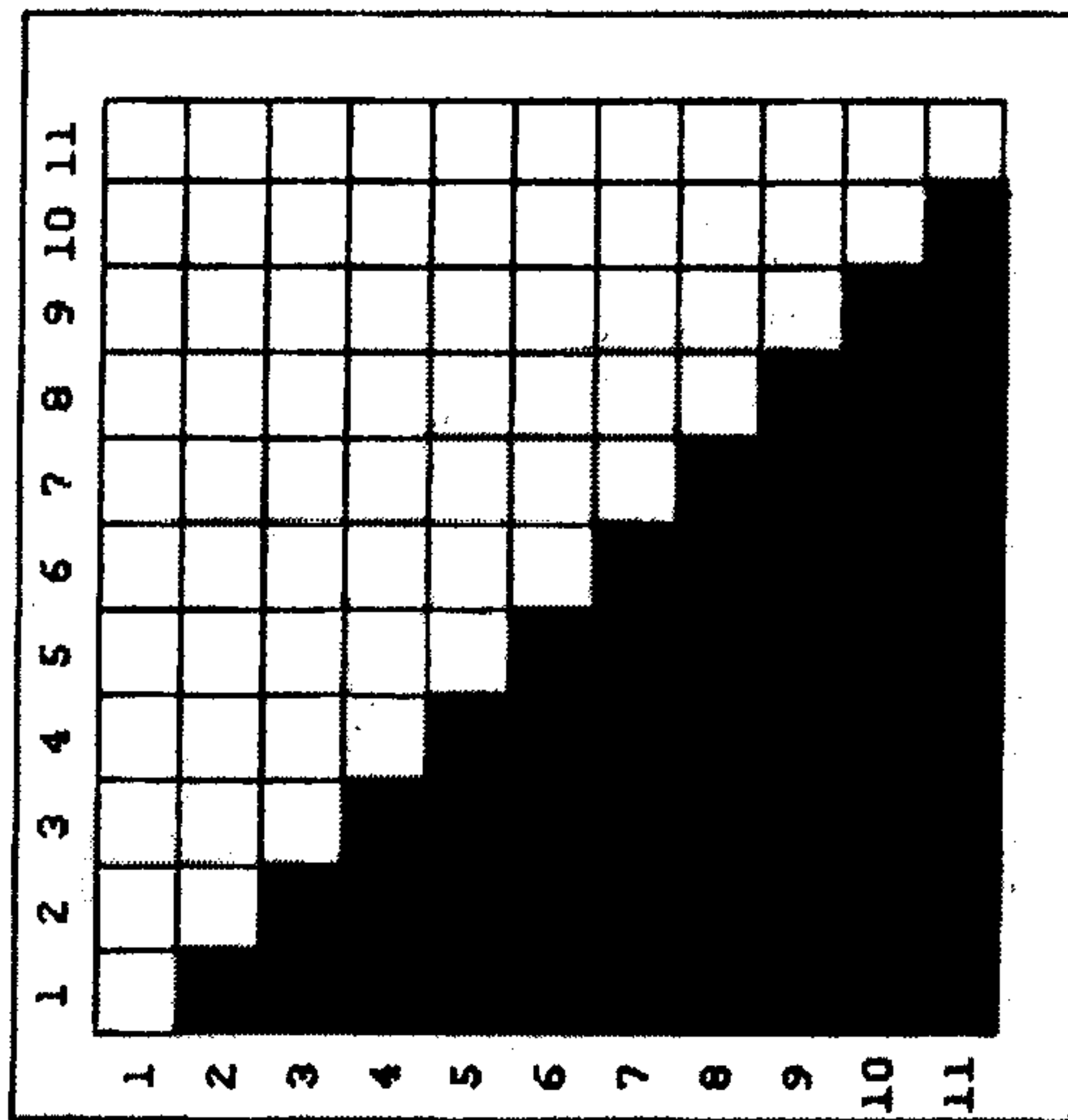
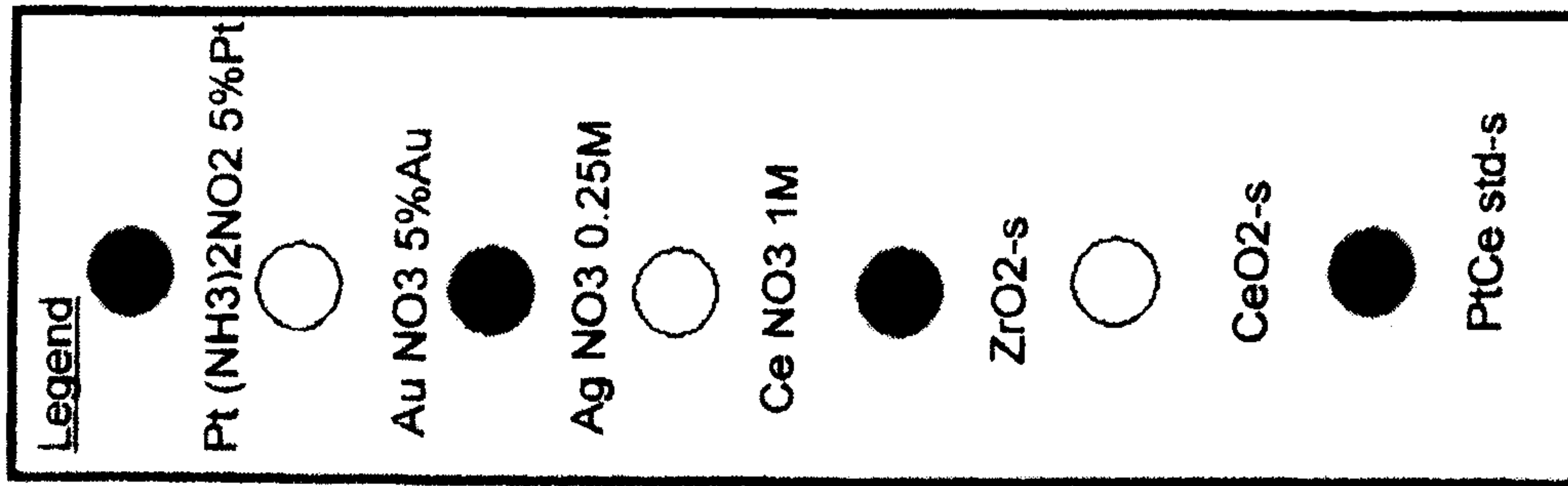


FIG. 9 D

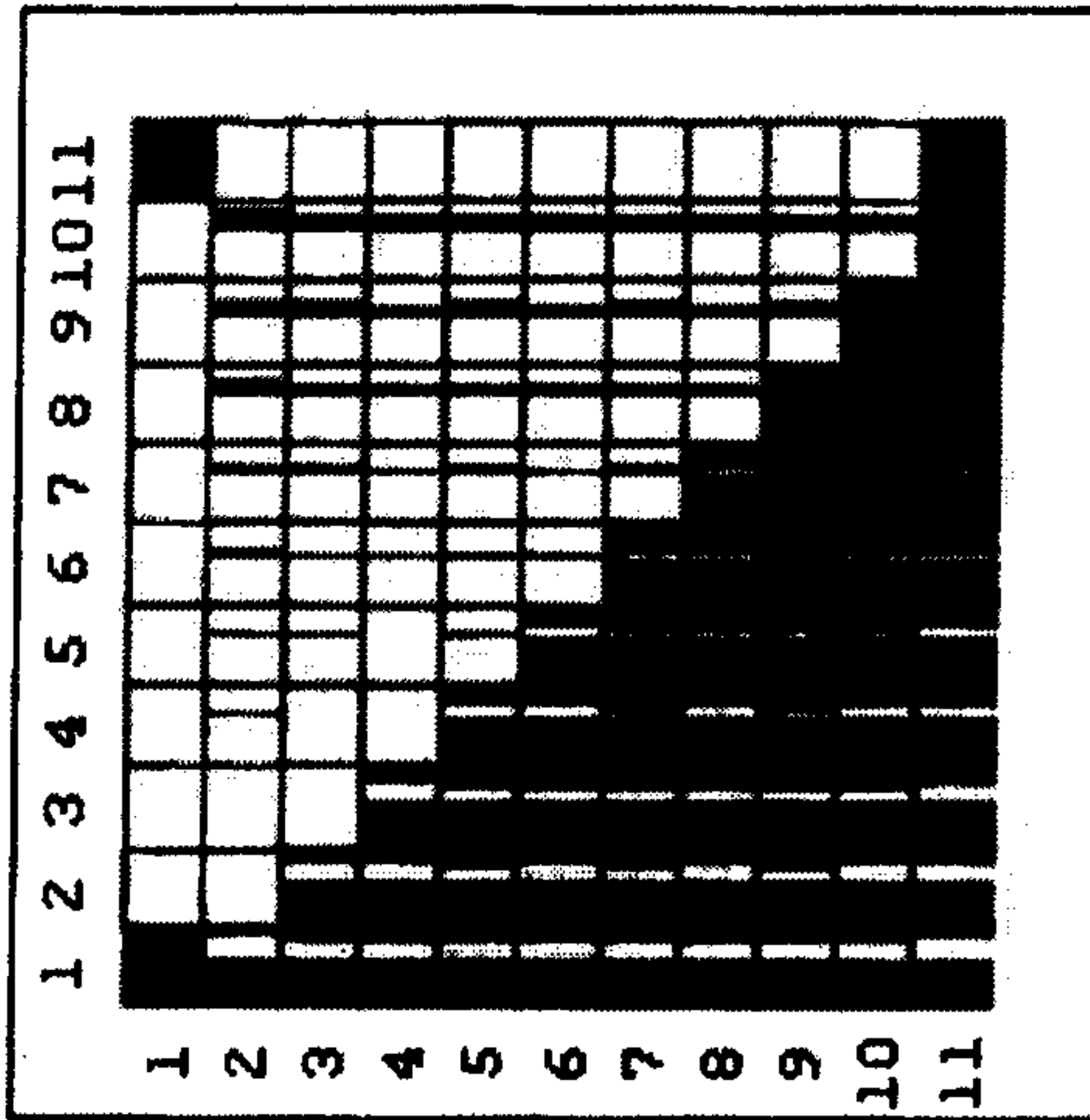
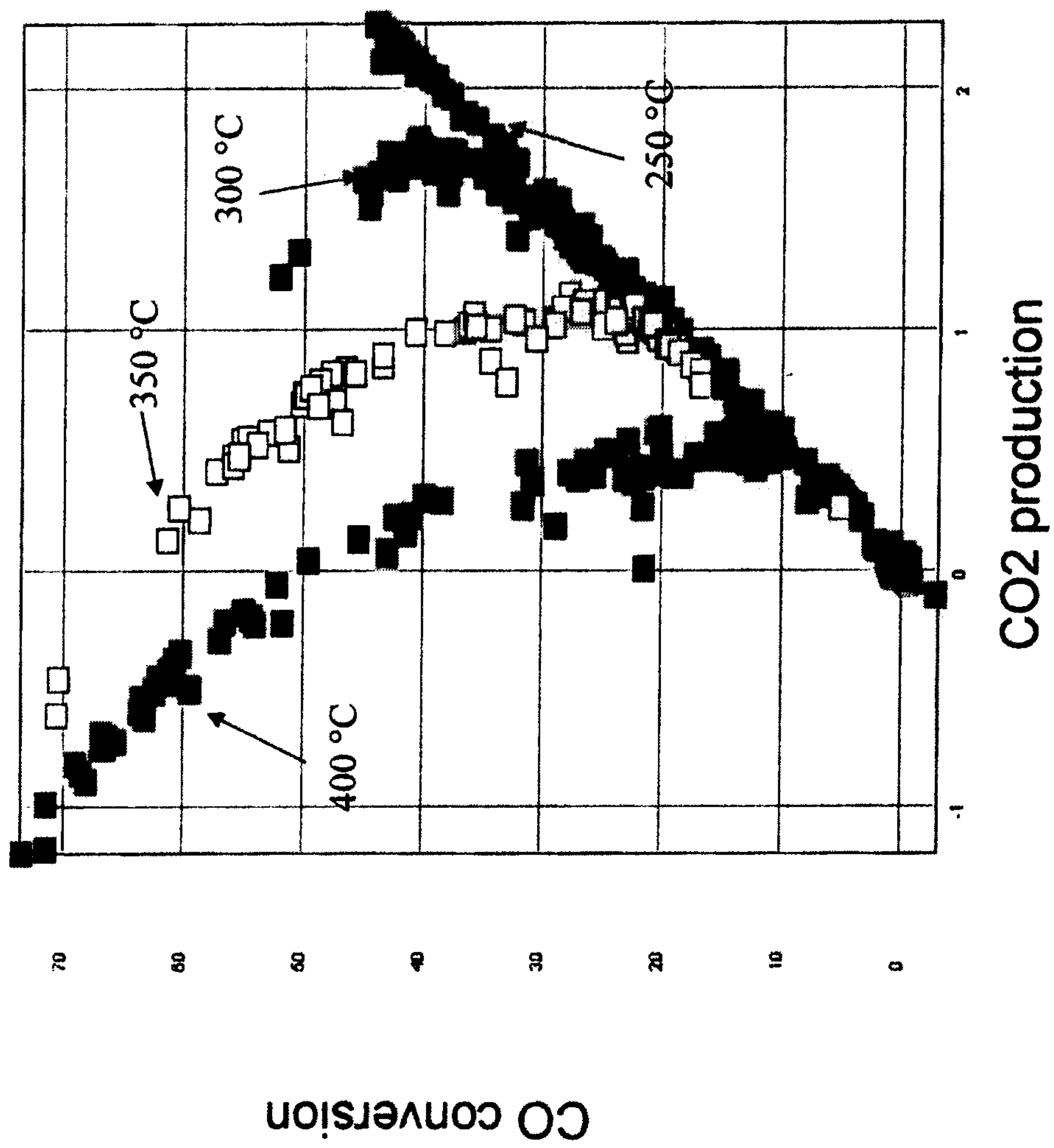


FIG. 9 E

FIG. 9 F

37/43

FIG. 10 A



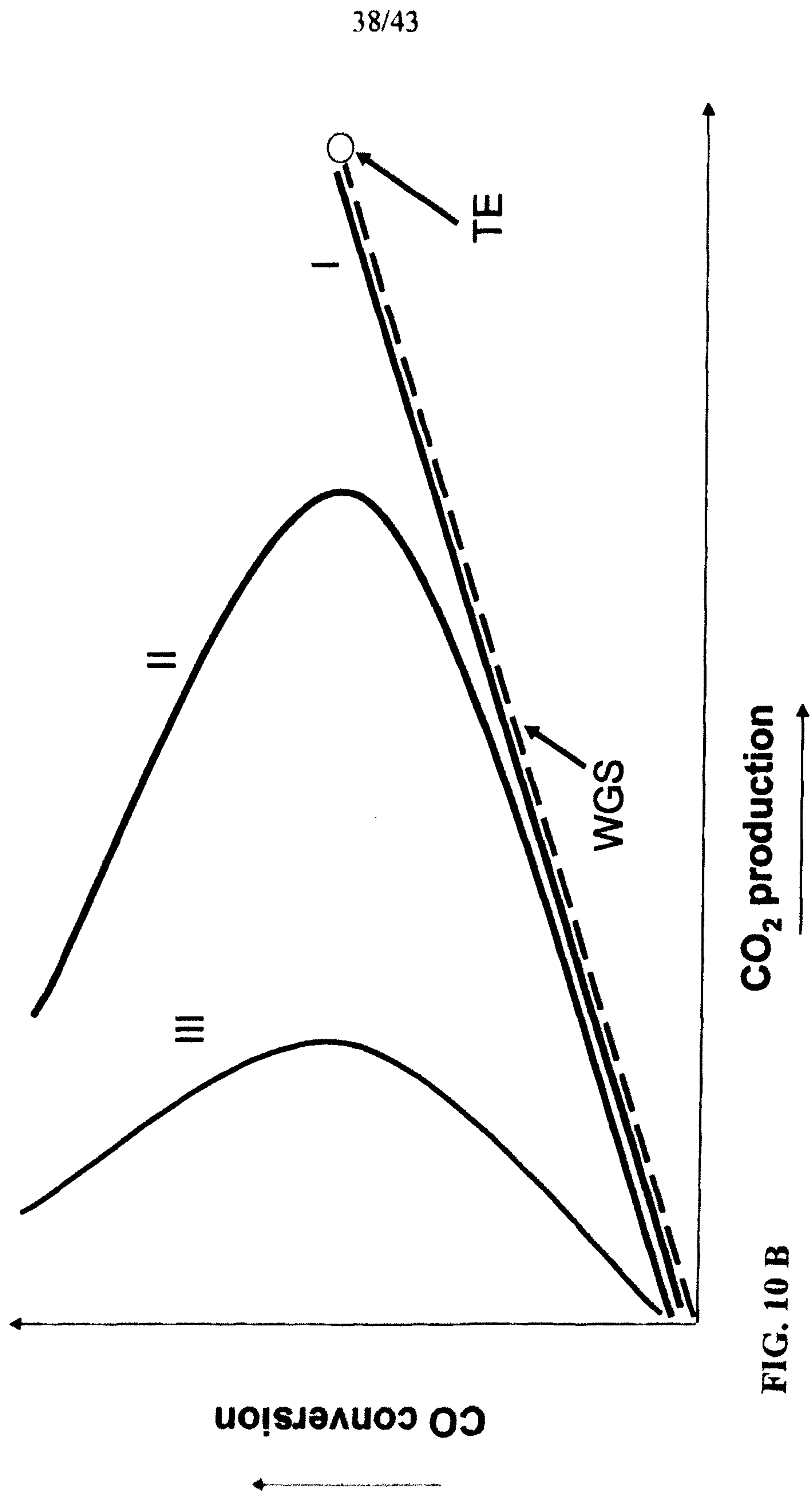
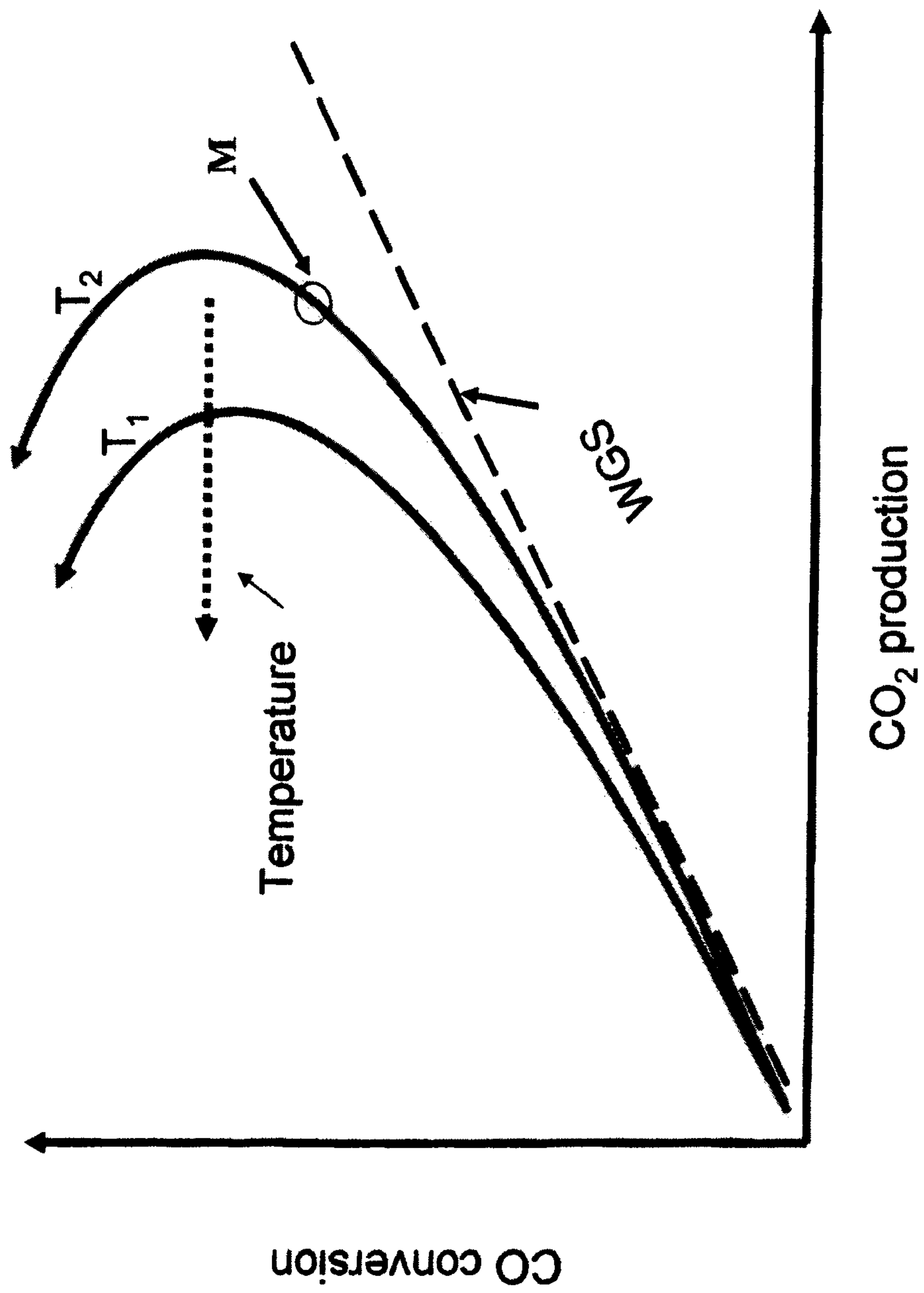


FIG. 10 B

39/43

FIG. 10 C



40/43

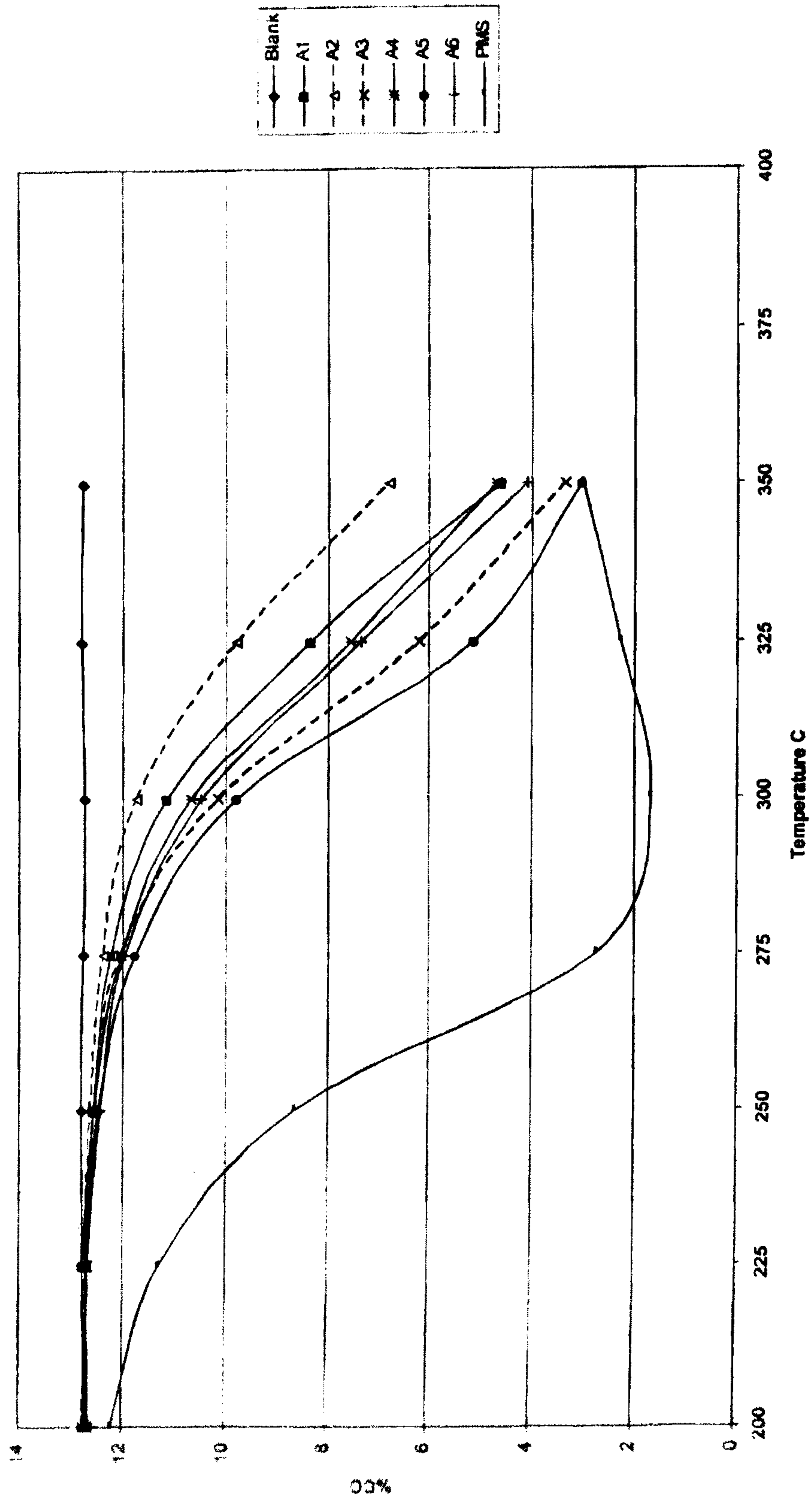


Fig. 11 A

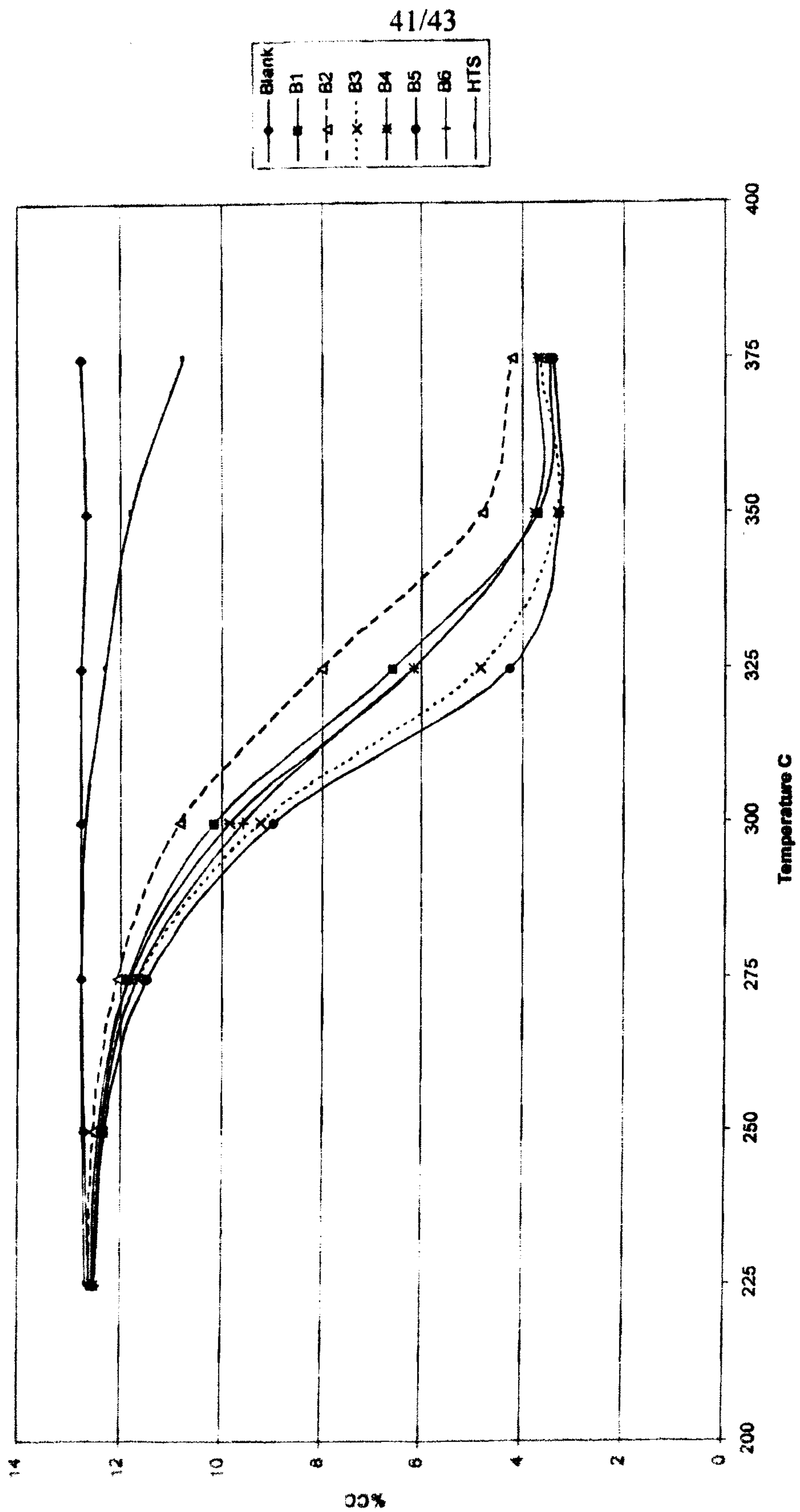


Fig. 11 B

42/43

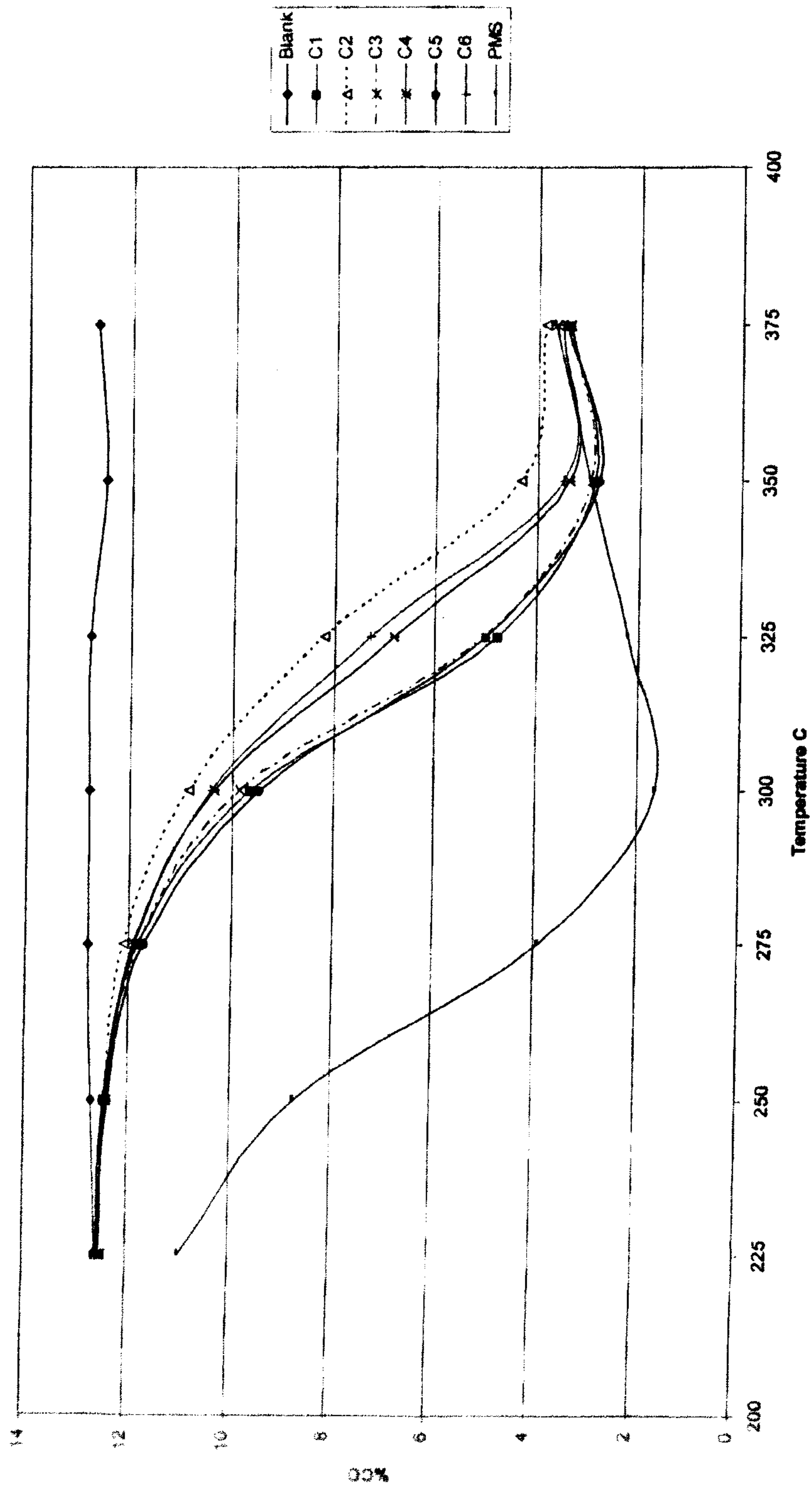


Fig. 11 C

43/43

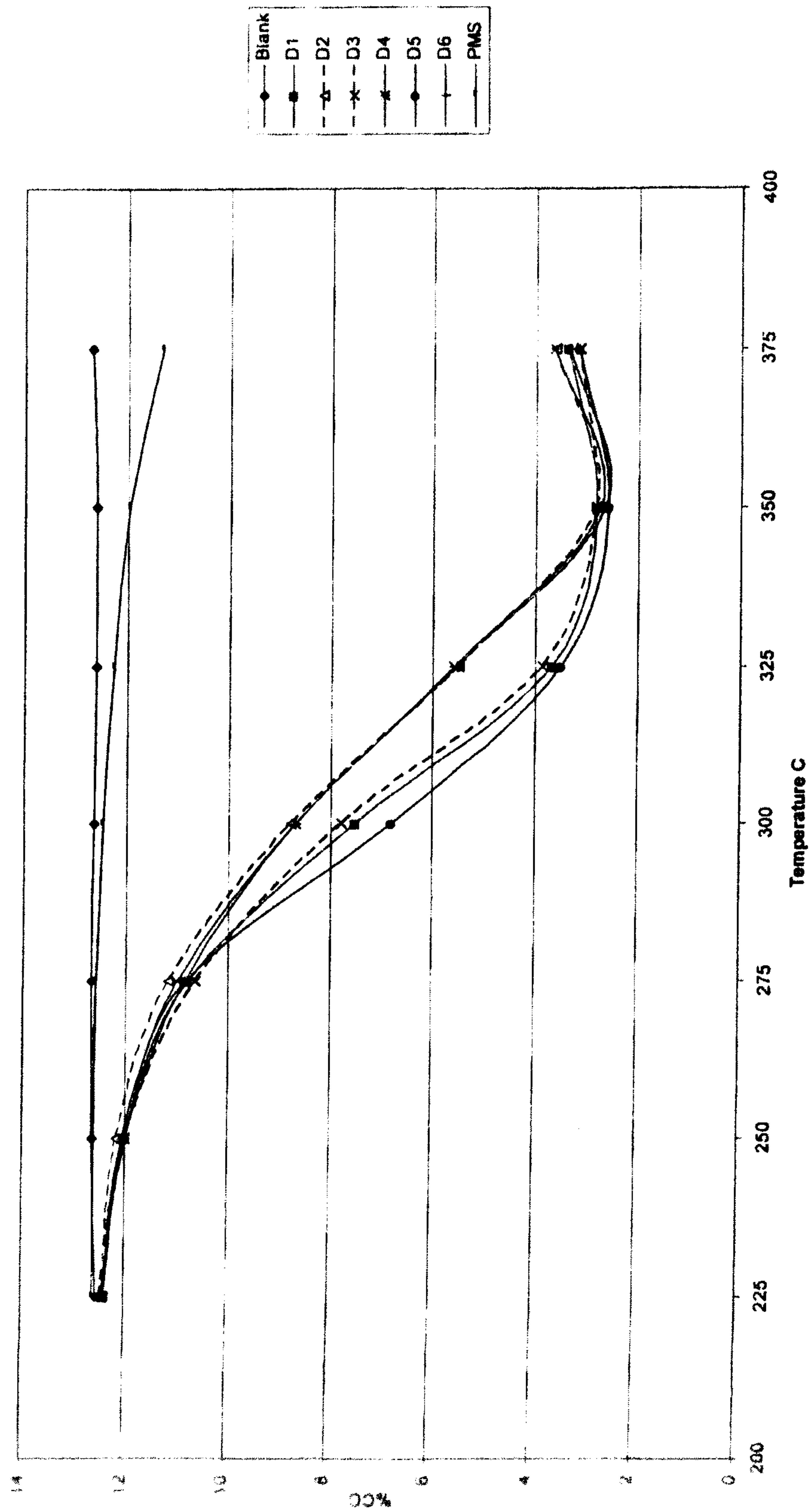


Fig. 11 D