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# THE EFFECTS OF GAS PHASE FORMALDEHYDE ON SELECTED INORGANIC MATERIALS FOUND IN MUSEUMS

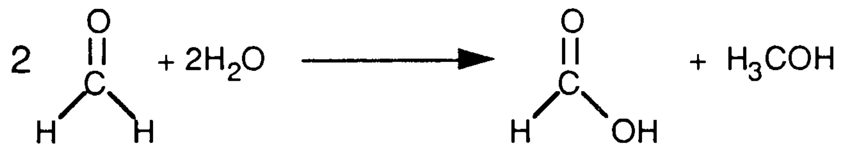
Mary F. Striegel[*]

## ABSTRACT

This paper presents the preliminary findings of a study on the potential damage of formaldehyde air pollution on inorganic materials similar to those found in museum collections. Glasses, ceramic glazes, shells and metals were exposed to 1200 parts per billion (ppb) of gas phase formaldehyde for 30, 60, and 100 day time intervals. Damage to materials was evaluated on the basis of changes in visual appearance after exposure to formaldehyde. Evidence of surface change was documented using optical microscopy, scanning electron microscopy, and color measurement.

## INTRODUCTION

Inorganic materials stored or displayed in museums may not be spared from the ravages of time. Pollutants within museums, such as acidic vapors or aldehydes released from wood and wood products, create corrosive environments which may damage inorganic objects (Hatchfield and Carpenter, 1987). Formaldehyde, which is found in museum environments, belongs to a class of chemicals known as aldehydes, and is characterized as having a hydrogen adjacent to a carbonyl group. Formaldehyde is a reducing agent. It can be oxidized to formic acid in the presence of water. This reaction (1), known as the Canizarro reaction, can be catalyzed on metal surfaces (March, 1977).



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Sources for formaldehyde include resins, wood products, particle board, plywood, construction materials, and combustion products (Committee on Aldehydes, 1981).

Information is needed on the potential for damage by indoor pollutants to museum collections. In order to answer this question, the Environmental Monitoring Program at The Getty Conservation Institute was designed. Seventeen institutions participated in the survey of indoor generated airborne pollutants including acetic acid, formic acid, formaldehyde and acetaldehyde (C. Druzik, Stulik, and Preusser, 1990)). The survey measured 183 individual sites within these institutions (galleries, storage areas and display cases). Concentrations of formaldehyde in museum environments range from less than 0.2 parts per billion to 1500 parts per billion. The question then became"what is the potential for damage to objects at these concentrations of pollutants ?" This study was designed to answer this question by exposing inorganic materials to gas phase formaldehyde.

## EXPERIMENTAL

### *Samples*

Replicate samples of all selected materials, including glasses, ceramic glazes, shells, and metals, were exposed to 1200 ppb of formaldehyde gas at a 30, 60, and 100 day time intervals. Two exposure samples and one control sample were investigated at each of the time intervals. The materials studied are listed in Tables 1A-1D.

### *Sample Preparation*

Eighty-one metal samples were prepared from nine different metal alloys, including copper, brass, bronze, silver, sterling silver, iron, tin, lead, and zinc. Most metals were cut into one inch squares, then mounted to glass slides and polished to a 0.25 micron finish. Tin and lead samples were ground to a 600 grit finish. Samples were then cleaned ultrasonically, rinsed with methanol, and dried in a cool air stream. After polishing, samples were stored in containers with desiccant and activated carbon.

Thirty-six stained glass samples were prepared from red, green, blue and yellow glass. One inch squares were cut by hand from plate glass supplied by a local stained glass supplier. Each sample was rinsed with methanol and dried in a cool air stream.

## TABLE 1A. MATERIALS STUDIED: GLASS.

| GLASS | COMPOSITION |
|---|---|
| Green | **Cu**, Cr |
| Blue | **Cu**, Co |
| Red | **Zn**, Cd |
| Yellow | **Ca, Mn** |

All glass was commercially available stained glass. Elemental composition was determined using X-ray florescence analysis. Elements in bold indicate major components, while plain text indicate minor components.

## TABLE 1B. MATERIALS STUDIED: SHELL.

| SHELL | COMPOSITION |
|---|---|
| Nautilus | $CaCO_3$ |
| Mexican Beige | $CaCO_3$ |
| MexicanWhite | $CaCO_3$ |
| Abalone | $CaCO_3$ |

The shells were not chemically analyzed; the composition indicated is the nominal composition for sea shells. Minor and trace elements were not determined.

## TABLE 1C. MATERIALS STUDIED: CERAMIC GLAZE.

| CERAMIC GLAZE | COMPOSITION |
|---|---|
| Green | **Cu, Pb**, Ca, Si, S |
| Blue | **Si, Pb, Co**, S, K |
| White | **Si, Al, Mg**, Ca |
| Black | **Si. Cr, Fe, Pb**, Ca, S, K, *Mn, Ni, Cu, Cd* |

Commercially available glazed ceramic tiles were obtained for this study. The composition was determined by energy-dispersive spectroscopy (EDS) on an Electroscan environmental scanning electron microscope (ESEM) using a Link Analytical system. Elements in bold indicate major components, plain text indicate minor components, and italics indicate trace components.

## TABLE 1D. MATERIALS STUDIED: METALS AND ALLOYS.

| ALLOY | COMPOSITION |
|---|---|
| Copper | 99.9% Cu |
| Brass | 70% Cu, 30% Zn |
| Bronze (cast) | 85% Cu, 5% Sn, 5% Zn, 5% Pb |
| Silver | 99.99% Ag |
| Sterling Silver | 95% Ag, 5% Cu |
| Lead | 99.99% Pb |
| Tin | 98.8% Sn |
| Zinc | 99.7% Zn |
| Iron | 99.5% Fe |

Composition for alloys given as nominal composition by supplier. The composition of bronze was verified using quantitative X-ray fluorescence Analysis.

Thirty-six glazed ceramic samples were cut from four different glazed ceramic tiles. Each two inch ceramic tile was cut into nine samples using a slow speed diamond saw. Samples then were rinsed with methanol and dried in a cool air stream.

Thirty-six samples of four types of seashells were selected and prepared for the formaldehyde exposure studies. These included Mexican white shells, Mexican beige shells, green nautilus shells, and abalone. The shells were prepared in the same manner as the ceramic tiles.

All samples were assigned a designation number which was then mechanically or hand engraved into the sample. The choice of control and exposure samples and time interval for each material was randomized by drawing lots. The samples were then placed in numbered locations in one of the chambers using randomly generated number tables.

### *Experimental Conditions*

The samples were exposed under conditions similar to those found in actual museum environments. Conditions for this study are given in Table 2. Target conditions selected were 50% relative humidity (RH), ambient temperature, and 1200 ppb formaldehyde in a dynamic system with a flow rate of 0.5 liters per minute.

The formaldehyde concentration was generated using a permeation device consisting of paraformaldehyde in a semi-permeable membrane. The permeation device was placed inside a glass U-tube in a warmed oven, and attached to the exposure flow system (Figure 1). Laboratory air was first cleaned and dried through a series of purification cartridges. The air stream was then split into two portions, one which was supplied to the permeation device and a second which was humidified. The humidified air stream was then split a second time -- one portion supplied cleaned, humidified air to the control chamber, the second was mixed with the formaldehyde air stream in a Teflon mixing chamber. From the mixing chamber, the formaldehyde air stream was passed through the exposure chamber, then cleaned with activated carbon, and finally exhausted. The experimental parameters of flow rate and oven temperature were adjusted until the monitored formaldehyde concentrations ( determined by HPLC methods (C. Druzik and Taketomo, 1988)) were approximately 1000 ppb formaldehyde at the inlet and outlet of the exposure chamber.

The formaldehyde concentrations were monitored throughout the 100 day exposure at both the inlet and the outlet of the exposure chamber, as well as at the outlet of the control chamber. Concentrations were monitored on a daily

TABLE 2. EXPERIMENTAL CONDITIONS.

The following conditions were controlled and monitored throughout the 100 day exposure:

| CONDITION | UNIT | MONITORING PERIOD |
|---|---|---|
| Relative Humidity | 50 ± 5% R.H. | 20 min |
| Temperature | 25 ± 4% ° C | 20 min |
| Formaldehyde | 1.2 ppm | daily 1st week; weekly |
| Flow rate | 0.5 L/min | |

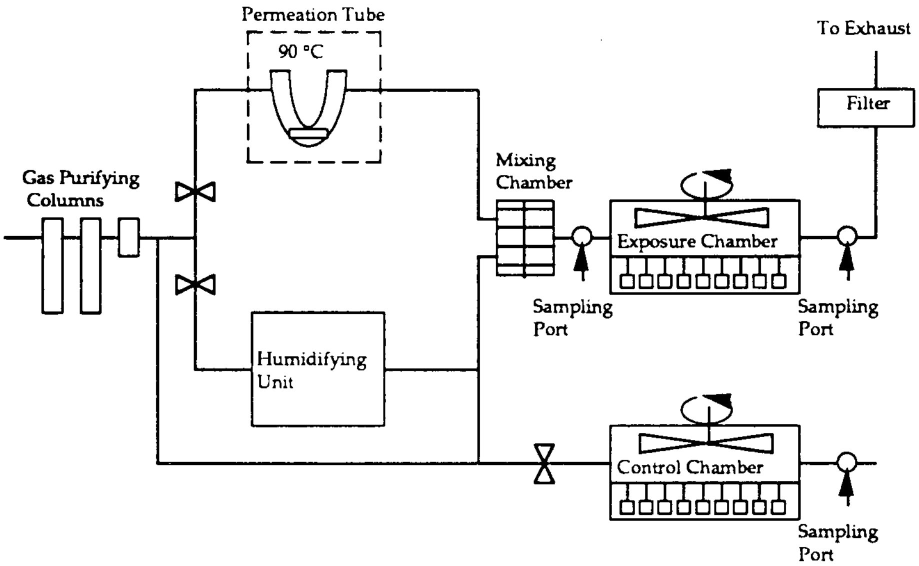

FIGURE 1. Schematic diagram of dynamic exposure system. Components include gas purification, permeation system, humidifying system, exposure chamber and control chamber.

basis for the first week of the exposure and weekly thereafter. Temperature and RH were monitored in 20 minute intervals throughout the experiment in the exposure and control chambers.

### *Instrumentation*

Samples were investigated with one or more of the following techniques:

Light Microscopy: All samples were examined after exposure by light microscopy using a Nikon Epiphot metallurgical microscope system. Samples which indicated an initial difference from the control sample of the same material and time interval were documented with bright field and dark field illumination.

Environmental scanning electron microscopy: Sample morphology and composition was investigated using an Electroscan environmental scanning electron microscope (ESEM) equipped with a Link Analytical Energy-dispersive spectroscopy system.

X-ray fluorescence Analysis: Initial compositions of some materials were verified using a Kevex 0750A secondary target X-ray fluorescence Spectrometer.

Color Measurements: Color measurements of glass and ceramic glazes were performed using a Minolta CR121 chromometer to support visual examination of samples. Four measurements were taken at corners of each sample both before and after exposure. Data was recorded in CIE-LAB units, and $\Delta E$ was calculated between pre- and post-exposure measurements. A series of standard color tiles were measured before and after each series of measurements on the samples in order to monitor any instrumental shifts.

## RESULTS AND DISCUSSION

After each exposure or control interval, all sample types were examined for evidence of change in surface appearance. Potential damage was assessed on the basis of change in visual appearance as evidenced by optical microscopy, color measurement, or electron microscopy. The results are given in Tables 3A-3D.

### *Glasses*

Two exposure samples and one control sample for each of the red, blue, green and yellow commercially available stained glasses were examined by optical

TABLE 3A.** RESULTS: GLASSES EXPOSED TO 1200 ppb FORMALDEHYDE GAS

| GLASS | 30 DAYS | 60 DAYS | 100 DAYS |
|---|---|---|---|
| Green | No | No | No |
| Blue | No | No | No |
| Red | No | No | No |
| Yellow | No | No | No |

Evidence of surface changes observed by optical microscopy.

TABLE 3B.** RESULTS: SHELLS EXPOSED TO 1200 ppb FORMALDEHYDE GAS

| SHELL | 30 DAYS | 60 DAYS | 100 DAYS |
|---|---|---|---|
| Nautilus | No | ?? | ?? |
| Mexican Beige | No | No | No |
| Mexican White | No | No | No |
| Abalone | No | ?? | ?? |

Evidence of surface changes observed by optical microscopy and scanning electron microscopy.

TABLE 3C.** RESULTS: CERAMIC GLAZES EXPOSED TO 1200 ppb FORMALDEHYDE GAS

| GLAZE | 30 DAYS | 60 DAYS | 100 DAYS |
|---|---|---|---|
| Green | No | No | No |
| Blue | No | No | No |
| White | No | No | No |
| Black | No | No | No |

Evidence of surface changes observed by optical microscopy and color measurement.

TABLE 3D.** RESULTS: METAL ALLOYS EXPOSED TO 1200 ppb FORMALDEHYDE GAS

| ALLOY | 30 DAYS | 60 DAYS | 100 DAYS |
|---|---|---|---|
| Copper | No | Yes | Yes |
| Brass | Yes | Yes | Yes |
| Bronze | Yes | Yes | Yes |
| Silver | ?? | ?? | Yes |
| Sterling Silver | No | Yes | Yes |
| Lead | Yes | Yes | Yes |
| Tin | ?? | ?? | ?? |
| Zinc | Yes | Yes | Yes |
| Iron | ?? | ?? | ?? |

Evidence of surface changes observed by Optical microscopy and scanning electron microscopy.

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** The criteria for entry into TABLE 3 is as follows: Yes = both exposed samples show a perceptible surface change from the control sample; ?? = one but not both samples show deviation from the control sample (or inconclusive results); and No = no perceptible change observed between exposed and control samples.

microscopy after exposure at 30, 60, and 100 day intervals. No visual changes were observed at 50x, 100x, or 250x magnification using both bright field and dark field illumination. In addition the color of each sample was measured in CIE-LAB units and ΔE was calculated between pre- and post -exposure measurements. No changes in surface appearance were found on any glass sample after 100 days of exposure to 1200 ppb of formaldehyde gas.

### *Shells*

Optical microscopy was used to investigate all shell samples after exposure. Although the irregular surfaces of the shells made comparison of control and exposure samples difficult, no surfaces changes after the 30 day interval were observed. After 100 days, the exposed and control samples of nautilus and abalone shells did show what may be efflorescence and were investigated further with ESEM analysis. Because the abnormalities on the surfaces could not be positively identified as efflorescence, and were seen on both the exposed and control samples, the results were considered inconclusive.

### *Ceramic Glazes*

The appearance of the glazed ceramic tiles was investigated with optical microscopy at 50x, 100x, and 250x magnification. Color measurements were performed in the same manner as for glass samples. No changes in surface appearance were found on any ceramic glazed sample after 100 days of exposure to 1200 ppb of formaldehyde gas.

### *Metals*

Changes in the appearance of the metal alloys were investigated using optical microscopy (at 50x, 100x, and 250x magnification) and Environmental scanning electron microscopy (at 1400x, 4200x, and 10,000x magnification). Of the materials tested, metal alloys showed the most sensitivity to formaldehyde exposure as seen in Table 3D. Four of the nine alloys investigated displayed conclusive visual changes after exposure to 1200 ppb formaldehyde in 30 days. These included brass, bronze, lead, and zinc. An additional three alloys, silver, tin, and iron, gave inconclusive results. By the end of the 100 day exposure, seven of the nine alloys showed definite changes from the control samples.

Based on visual results, copper and copper based alloys (brass and bronze) initially developed thin tarnish or corrosion films after formaldehyde exposure. Both copper and brass displayed corrosion films consisting of submicron particles that tended to congregate along scratches or deformations in the surface. But the rate of corrosion differed for these two metals. For the brass samples, initial corrosion films were seen after 30 days of formaldehyde exposure. The copper samples developed tarnish films after 60 days of exposure. The corrosion film found on the bronze samples after 30 days tended to be made up of individual particles randomly located on the surface. After 100 days exposure the corrosion film on all copper based samples tended to approach micron thickness in some areas. In addition, small corrosion blooms were found in pitted areas on the bronze samples. Visually, it appeared that two types of corrosion processes were active on the bronze samples. The nature of the films were not evident by particle shape. And the small size of the corrosion particles did not allow for characterization using X-ray diffraction techniques.

There was a possibility that paraformaldehyde used in the permeation device to generate the formaldehyde atmosphere may have precipitated out onto the sample surfaces. A simple test was performed to determine if the film was paraformaldehyde. A site on the surface of a 100 day exposure bronze sample was selected near a corrosion bloom, and a cross hatch was engraved as a reference marker. An electron micrograph of the surface was taken to document the site. Then, the sample was placed in a oven at 100 °C for 72 hours (at this temperature paraformaldehyde sublimes to formaldehyde gas). Re-examination of the sample site showed no change in the surface film, thus ruling out paraformaldehyde precipitation.

The bronze 100 day exposure sample was investigated further using energy-dispersive spectroscopy surface analysis. Analyses were performed at five locations as noted in Figure 2. Locations included areas with little corrosion and pitted areas which displayed corrosion blooms. The results of these analyses (given in Table 4) showed that the bronze alloy was heterogeneous. Lead tended to pool out of the alloy at pitted areas, resulting in low concentrations of lead at other locations on the surface. The formation of corrosion blooms in surface pits may indicate preferential attack by formaldehyde on lead within the alloy. Individual corrosion particles, similar in shape and size to those found on copper and brass samples, were seen at other locations on the sample where the concentration of copper was much higher. These facts support the premise that two corrosion processes may be taking place on the bronze alloys.

Silver and sterling silver displayed evidence of corrosion at a slower rate than the copper based alloys. Conclusive evidence of corrosion was found on sterling silver after 60 days and on pure silver after 100 days of exposure. Sub-micron corrosion particles were seen on both materials. However, on the sterling silver these particles tended to form islands approximately 5 microns in size. The islands were grouped near deformation sites. A discontinuous corrosion film was formed by individual particles on the pure silver samples.

TABLE 4. EDS ANALYSIS OF EXPOSED BRONZE SAMPLE SHOWING HETEROGENEITY.

| LOCATION | % COPPER | % TIN | % ZINC | % LEAD |
|---|---|---|---|---|
| 1 | 6.4 | 1.1 | 0.6 | 92.1 |
| 2 | 7.4 | 0.4 | 0.7 | 91.8 |
| 3 | 90.7 | 5.1 | 3.2 | 0.5 |
| 4 | 92.3 | 2.6 | 3.4 | 1.7 |
| 5 | 92.9 | 3.1 | 3.6 | 0.4 |

EDS analysis performed on Electroscan Environmental Scanning Electron Microscope using a Link Analytical System. Instrumental conditions: 20 kV, 150 μA beam current, beam size 30, 25 ° sample tilt.

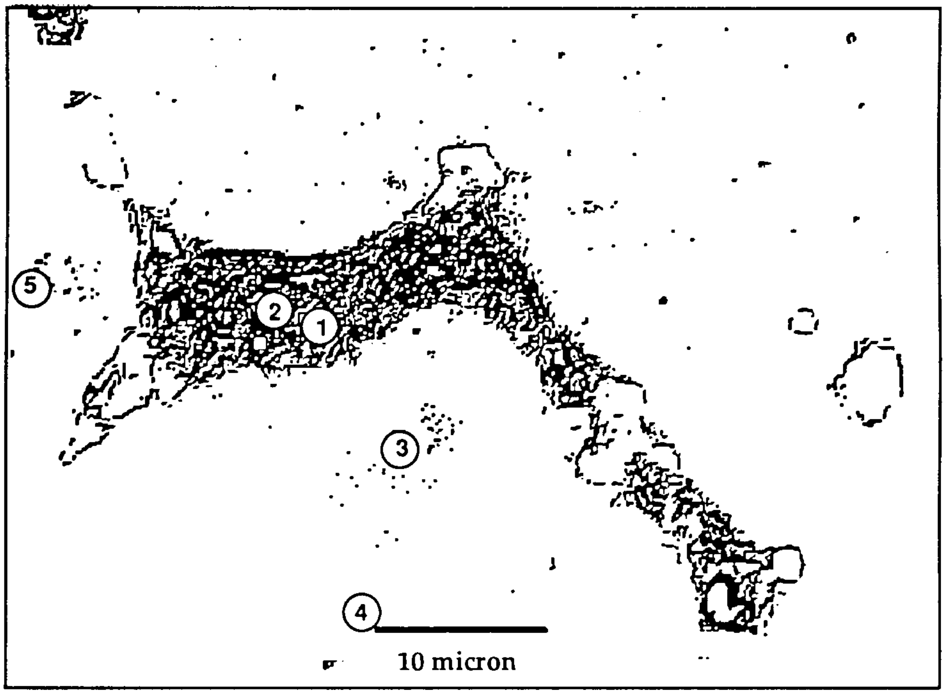

FIGURE 2. Illustration showing the locations of EDS analysis on exposed bronze sample (see TABLE 4). Each location is marked by a circle containing the location number. 1450 x magnification. The black areas designate corrosion on the surface of the bronze. Corrosion took place preferentially in pitted areas and areas of high lead concentration.

Zinc corrosion films were also seen upon exposure to formaldehyde. The corrosion was first observed after 30 days of exposure. The film was made up of sub-micron banana or propeller shaped crystals, similar in morphology to zinc oxide. This type of film was not seen on the control samples, which may indicate an acceleration of zinc oxide formation in the presence of formaldehyde. However, the identification of zinc carbonates or formates as the corrosin product cannot be ruled out.

The results of formaldehyde exposure on tin and iron were inconclusive. Although signs of corrosion were seen on exposed samples for each material, similar corrosion was also found on the control samples. The possible role of formaldehyde in the corrosion processes could not be determined.

Corrosion products were also found on surfaces of exposed and control samples of lead after all exposure time intervals. The corrosion films were readily seen in dark field illumination by optical microscopy and by electron microscopy. The crystalline particles of the corrosion films on the exposed and control samples differed significantly. Tetragonal particles with occasional needles were found on the control samples, while columnar groupings were observed on the exposed samples. A standard lead sample containing basic lead carbonate crystals was compared to the exposed samples. Based on the morphology of the corrosion products the exposed corrosion film was tentatively identified as basic lead carbonate. The tetragonal particles found on the control samples may be lead oxide which readily forms on lead surfaces. It was not possible to identify the corrosion products by X-ray diffraction analysis.

## CONCLUSIONS

This survey investigation shows that, of the four types of inorganic materials studied, metals and metal alloys are most sensitive to 1200 ppb formaldehyde gas. Of the nine metals and alloys examined, seven showed apparent damage after 100 days of exposure to 1200 ppb of formaldehyde. Based on visual observations after 100 days exposure, the sensitivity of metals to formaldehyde (in decreasing order) is lead > bronze > brass > zinc > copper > sterling silver > silver. Inconclusive results were obtained on examination of tin and iron.

Other inorganic materials studied were much less susceptible to damage by exposure to formaldehyde. Although shells may be sensitive to formaldehyde exposure, the findings of this study do not conclusively indicate active formation of efflorescence at 1200 ppb of formaldehyde over a 100 day time interval. The commercially available stained glasses and ceramic glazes exhibited no visual changes after exposure to formaldehyde under these conditions.

The results presented in this paper represent preliminary findings. The chemical composition of corrosion products was not determined due to the nature of the thin corrosion films found. Future research may focus of chemical identification and quantification of these corrosion products, as a first step in elucidating the reaction mechanisms and materials damage functions upon exposure to concentrations of formaldehyde similar to that found in the museum environment.

## ACKNOWLEDGEMENTS

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## REFERENCES

Committee on Aldehydes. *Formaldehyde and Other Aldehydes.* National Research Council. (Washington DC, 1981).

Druzik, Cecily M., and Amy Taketomo. *Standard Operating Protocol for the Analysis of Airborne Aldehydes, Ketones and Carboxylic Acids Using HPLC.* Final report. The Getty Conservation Institute. (Marina del Rey CA, 1988).

Druzik, Cecily M., Dusan Stulik, and Frank Preusser. *Carbonyl and Organic Acid Pollutants in the Museum Environment.* Presented in the Objects Specialty Group, Annual Meeting of the American Institute for Conservation, 1990, Richmond, VA.

Hatchfield, Pamela, and Jane Carpenter. *Formaldehyde: How great is the danger to museum collections?.* Center for Conservation and Technical Studies. (Boston MA, 1987).

March, Jerry. *Advanced Organic Chemistry, Reactions, Mechanisms, and Structure.* McGraw-Hill. (New York, 1977): 1139-1140.