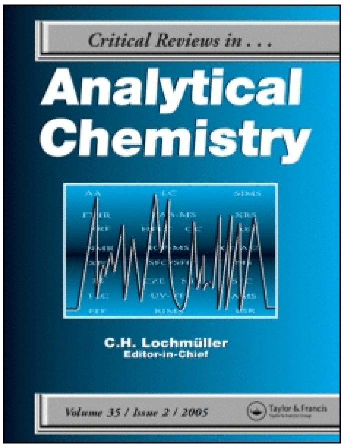

Critical Reviews in Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

Positron Annihilation Spectroscopy for Chemical Analysis

K. L. Cheng[a]; Y. C. Jean[a]; X. H. Luo[a]
[a] Department of Chemistry, University of Missouri, Kansas City

To cite this Article Cheng, K. L. , Jean, Y. C. and Luo, X. H.(1989) 'Positron Annihilation Spectroscopy for Chemical Analysis', Critical Reviews in Analytical Chemistry, 21: 3, 209 — 224

To link to this Article: DOI: 10.1080/10408348908050844

URL: http://dx.doi.org/10.1080/10408348908050844

Positron Annihilation Spectroscopy for Chemical Analysis

K. L. Cheng, Y. C. Jean, and X. H. Luo

I. INTRODUCTION

The prediction and discovery of the existence of positron $(e^+)^{1-4}$ and positronium atom $(Ps)^{5,6}$ led rapidly to the development of a new spectroscopic technique for the study of the structure and composition of matter. The technique quickly expanded across interdisciplinary from physics to chemistry, metallurgy, biochemistry and recently to superconductors. As an early non-destructive and *in situ* testing tool, positron annihilation spectroscopy (PAS) has been utilized extensively to measure crystal defects.[7-9]

The theory and applications of PAS have been presented in several monographs and in a number of reviews[10-12] on applications to chemical studies. A brief review of the literature reveals that the development of PAS has been made in several stages. Its development may be summarized in Table 1.

Many physics discoveries became obscure due to lack of applications. On the other hand, Mass Spectroscopy, NMR, Activation Analysis, Photoelectron Spectroscopy (ESCA), IR, Auger Electron Spectroscopy (AES), etc. have all been well known mainly due to their important analytical applications. Physicists discover the phenomena and then analytical chemists use them. Now, it is the time when these chemists use their knowledge to kindle their interests, to refine this new technique, as well as to find out more applications for various samples.

Among many new instrumental techniques added to the chemists' arsenal, positron annihilation spectroscopy for chemical analysis (PASCA) is one of the most ideally suited to surface studies. It is sensitive and quantitative.

This review gives an overview of PASCA with the particular emphasis on those aspects related to surface analysis. Sections on fundamentals and instrumentation are found in other reviews. We coined the term PASCA, because we wish to emphasize the importance of the analytical applications of PAS with respect to quantitative surface characterization. Furthermore, the term PASCA was proposed for avoiding confusion with the technique known as PAS (photo-acoustic spectroscopy).

Table 1
History of Positron Annihilation Spectroscopy Development

1930s	Prediction of positron existence by Dirac.[1] Discovery of e^+ by Anderson.[2-4] Existence of Ps by Deutsch.[5,6]
1950s	Structure and properties of e^+ and Ps by physicists.
1960s	Applications of e^+ and Ps to study condensed matter by physicists.
1970s	Chemical applications of e^+ and Ps by physical chemists.
1980s	Quantitative PAS (PASCA) by analytical chemists.

According to the difference of positron sources, positron annihilation spectroscopy may be divided into two categories: fast positron annihilation spectroscopy and slow positron spectroscopy. Slow positrons may be generated from ^{22}NaCl with an activity of ~25 mCi. Together with a tungsten (or molybdenum) moderator, the system allows a flux of slow positrons of up to about 2×10^5/s along with an energy spread of about 4 eV. These positrons may be accelerated to an energy of 200 eV. The slow positrons have found increasing applications to the solid state science, particularly to surface adsorption and desorption. However, this slow positron technique requires high vacuum and will be *ex situ*. This review is confined to the description of fast positron annihilation technique.

Because PASCA is a relatively new analytical technique, the literature is undergoing a rapid expansion. Applications of PASCA to surface studies have only begun to appear; it is safe to predict that these analytical applications will progress much faster when a commercial instrument package of PASCA is readily available. Therefore, this review should be viewed as an illustration as to the type of surface studies possible by PASCA, rather than a compendium of neatly completed results.

II. *EX SITU* AND *IN SITU* TECHNIQUES

The field of surface science and interfacial phenomena is one of the most exciting areas of research today. The importance of these various surface chemical processes occurring at the solid-solid, solid-liquid, solid-gas, liquid-liquid, and liquid-gas interfaces has been realized now for several decades. By using a variety of sophisticated analytical methodologies to characterize the chemical and structural changes of solid surfaces, this field of research has been revolutionized in the past decades. At least a dozen of new surface techniques have been developed by using ultra-high vacuum and electron counting systems. It is customary to classify surface analytical methods into areas of study involving solid-gas, solid-liquid, and solid-solid interfaces. Many surface techniques cause a different degree of perturbation due to the interactions between the incident beam of particles and the sample under study. These chemical methods can be categorized into two types: (1) *ex situ* methods and (2) *in situ* methods according to the degree of perturbation (see Table 2).

One of the most active research areas in surface and interface science is to search for non-destructive and *in situ* techniques. The most significant advantage in such techniques

K. L. Cheng received his B.S. from Northwestern College, China and his M.S. and Ph.D. from the University of Illinois, Urbana. Currently Dr. Cheng is Professor of Chemistry in the Department of Chemistry, University of Missouri, Kansas City. **Y. C. Jean** earned a Ph.D. from Marquette University, Milwaukee, Wisconsin. Dr. Jean is Professor of Chemistry and Physics in the Department of Chemistry, University of Missouri, Kansas City. **X. H. Luo** is with the Departments of Chemistry and Physics, University of Missouri, Kansas City.

Table 2
Comparison of Surface Characterization Techniques

Technique	Incident beam	Detected particle	Category
LEED			
EELS			
HREELS	e^-	e^-	*Ex situ*
IETS			
AES			
USP			
XPS (ESCA)	hγ	e^-	*Ex situ*
SEXAFS			
ISS			
SIMS	M^+	M^+	*Ex situ*
Rutherford			
IR-Reflectance			
Raman	hγ	hγ	*In situ*
Surface enhanced Raman			
Ellipsometry	Polatized hγ	hγ	*In situ*
PELS			
LEPD	Slow e^+	2γ or 3γ	*Ex situ*
PAS or PASCA	Fast e^+	2γ or 3γ	*In situ*
Neutron scattering	n -	n	*Ex situ*

is that they can be used to investigate practical or real world systems such as catalysts in finely divided powders and porous forms, in electrochemical systems involving solvents[78] or in foams.[77]

When photons, ions, electrons, or neutrons are used as probes, they, being in contact with the surface of a sample, undergo changes in their properties, such as diffraction, reflection, scattering, etc., resulting in energy shifts or loss of probing particles. In utilizing these techniques, an ultra-high vacuum (UHV, $< 10^{-9}$ torr) is often required.

There have been very few surface techniques which can really be considered as *in situ* methods. The most important and widely used *in situ* methods are IR reflectance spectroscopy, ultrasound, and ellipsometry. In general, *in situ* techniques are non-destructive and deal with photon emission requiring no high vacuum. The development and application of novel *in situ* techniques would contribute significantly to the understanding of a variety of processes involved in industrial catalysis and electrochemical reactions and biochemical changes. PASCA can be performed at high or low temperature, in vacuum or at high pressure. It is an *in situ* surface technique.

III. HIDDEN SURFACE

In catalyst systems, the internal pore structure of the support hides the metal particles and poses a difficulty in studying their structures, oxidation states, and compositions, which determine their activity and selectivity. Characterization of these complexes in practical systems cannot be done with *ex situ* techniques since there may exist a number of catalytically active sites which are inaccessible and hidden in tortuous pores or "caves" (see Figure 1).

Development of a surface technique which is *in situ* and sensitive to hidden active sites is valuable to the surface and interfacial research.

IV. LIFETIME

A positron lifetime spectrum represents the disappearance of positrons in the system. Since the electronic time measurement begins when a positron is formed, the spectrum may be viewed in terms of a large number of positrons being initially present in the sample, bouncing back to the surface and void due to the negative work function of positron,[13,14] and disappearing through annihilation by various processes. Each mode of annihilation is characterized by an annihilation rate constant, which is the reciprocal mean lifetime, τ, of the positron.

The Ps-molecule complex formation can be evaluated quantitatively by setting up the appropriate kinetic equations:[15,16]

$$2\tau \xleftarrow{\lambda_1} \text{o-Ps} + \text{M} \underset{K_2}{\overset{K_1}{\rightleftharpoons}} \text{Ps-M} \xrightarrow{\lambda_2} 2\tau$$

where λ_1 is the Ps annihilation rate constant with the solvent; λ_1 is the Ps-M complex annihilation rate; and K_1 and K_2 are the formation and dissociation rate constants for the Ps-M complex, respectively. Substances with high electron affinities such as halogens, oxygen, and nitroaromatics show a strong reactivity with Ps. They have been frequent subjects being studied by PASCA.

The lifetime spectrum may have as many as τ_1, τ_2, . . . τ_7, but for most samples, the lifetime spectrum is resolved into 2, 3, or 4 components. Namely, τ_1 (λ_1) and I_1 represent the annihilation in the bulk, τ_2 (λ_2), and I_2 represent the annihilation on the surface, while τ_3 (λ_3) and I_3 represent the annihilation in the void. The intensity (I) of the lifetime component rep-

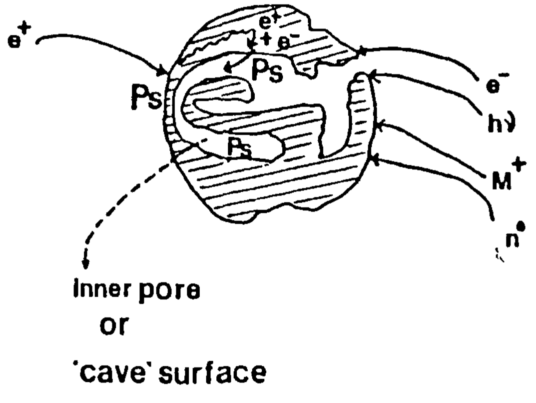

FIGURE 1. Cave surfaces.

resents the probability of e^+ or Ps formation. The lifetime spectra are recorded by a multichannel analyzer and deconvoluted by using a computer program such as POSITRONFIT EXTENDED.[17]

The results of τ (λ), or I often provide a quantitative relationship with the composition of sample profile in the bulk, on the surface, or in the void.

V. PASCA AS A QUANTITATIVE TECHNIQUE

Many surface techniques such as ESCA[18] and AES [19] are semi-quantitative because several factors affect the quantitative response due to adsorption, or scattering of emitting particles. However, for the positron or Ps annihilation processes, these effects are minimum. The following relationship holds with relatively simple parameters:[10]

$$P = P^o/[1 + K(M)]$$

where P^o and P are the o-Ps formation probability for the pure solvent and the solution, respectively; K is the rate constant for inhibition of o-Ps formation with [M] being concentration of solute. This relationship is also applied to solids with the K value being different for various materials. Both Figures 3 and 4[21] illustrate the quantitative relationship.

The PASCA can also determine the percent of major components or the impurities in ppm levels:

$$\lambda_v = \lambda_v^o + K_v[M]_v$$

$$\lambda_s = \lambda_s^o + K_s[M]_s$$

$$I_s = I_s^o + K_s[M]_s$$

The subscripts v and s signify o-Ps annihilation rate for void and surface, respectively. It appears that the λ and I values are proportional to the concentration of M (solute).

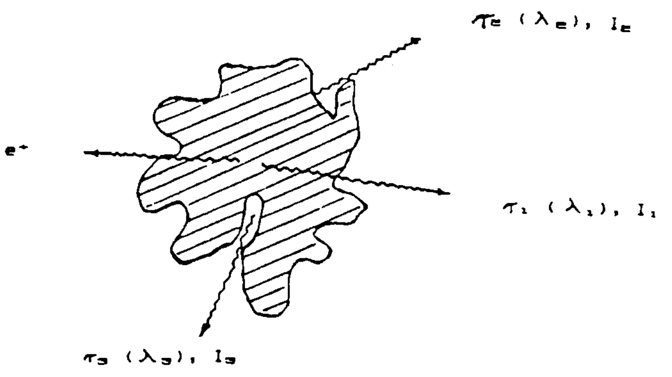

FIGURE 2. Lifetimes of positron and positronium.

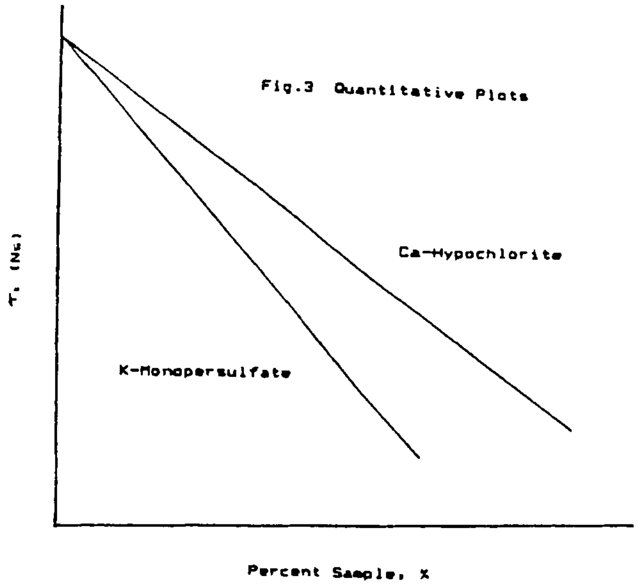

FIGURE 3. Quantitive plots of oxidants.

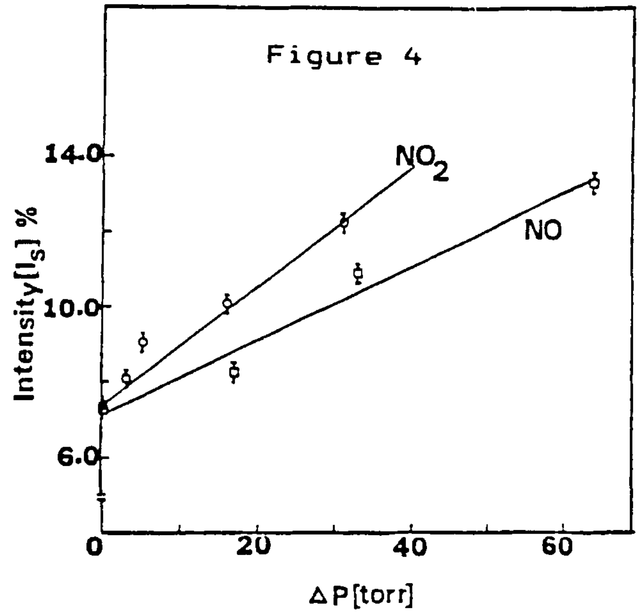

FIGURE 4. Effect of nitrogen oxides on intensity.

VI. DETERMINATION OF TOTAL SURFACE AREA

One of the important considerations in catalysis is the need to provide a large contact area between the reactants and the surface. A catalyst with high enough surface area will provide enough space for catalytic components (metals or non-metals) to disperse onto it. In general, surface area is related to the number of active sites located on the surface of the catalysts.[22] Measurement of the surface area of powders and porous materials requires indirect methods, including[23]

BET method
Dye adsorption
Fatty acid adsorption
Calorimetric method of Harkins and Jura
Soap titration method

The most common technique is that devised by Brunauer, Emmett, and Teller, known as the BET method.[24] The sample, placed in an evacuated tube along with inert gas (usually N_2), is introduced into the closed volume containing the sample. The change in pressure, due to adsorption, is measured with a McLean or calibrated Pirani gauge. This is done with the sample both at room temperature and at liquid nitrogen temperature, the latter by raising a Dewar containing liquid nitrogen around the tube containing the sample. Theoretically, up to a monolayer of nitrogen will be physically adsorbed at 77 K, and hence from the drop in pressure and known volume, the quantity of adsorbed nitrogen molecules and therefore the surface area may finally be deduced.

If the surface area exceeds 50 cm^2, errors coming from adsorption on the unavoidably cooled walls of the tube will, nevertheless, be small, and can be estimated and corrected from a blank. Also errors can arise from factors such as fitting of a straight line to the experimental points and imperfect applicability of the basic theory. For instance, the value of the effective area as covered by nitrogen molecules may vary. There are many inaccessible hidden areas, which nitrogen molecules can not diffuse into and hence can not adsorb onto. In practice, an error of up to 100% can be considered to be possible. BET is a widely used method today.[25]

It is known that certain samples such as alumina and zeolites are not suitable for BET method.[26] Obviously, an alternative and better technique is needed for the determination of total surface areas for samples, particularly for alumina and zeolites. The positron annihilation technique for total surface area determination has been developed consequently.[27] Unlike other techniques based on the adsorption, the positron annihilation is based on the linear correlation between the intensity of long-lived Ps component, I_3, and the surface area. Neither gas nor liquid is introduced into the sample. o-Ps atoms tend to be trapped at the surface and voids with intensity depending on the surface area. Figure 5[27] demonstrates a linear relationship for various types of samples. The positron technique may, in part, prove to be very useful to supplement the BET method. We found that a linear curve fits fairly well for all systems except at very low surface areas (<70 m^2/g). In order to use this universal slope for a surface determination, an empirical linear equation for two different regions of surface areas may be suggested. The best-fitted equations are[27]

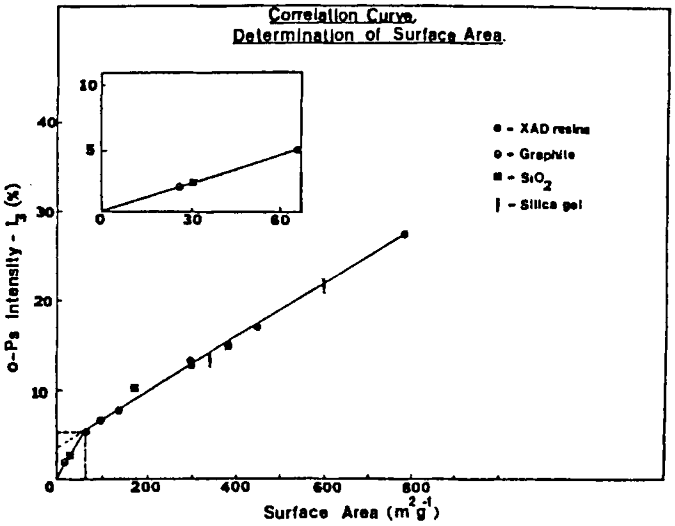

FIGURE 5. Correlation between surface area and o-Ps lifetime.

$$I_0 = 3.0 + 0.0335 \times S \qquad (>70\ m^2/G)$$

$$I_3 = 0.080 \times S \qquad (<70\ m^2/G)$$

where S is the surface area (m^2/g) and I_3 is the observed longest lived o-Ps intensity in the media. It is also worthwhile to point out that the void concentration also correlates with I_3. The positron lifetime as a function of grain size has also been reported.[28]

VII. PORE SIZE AND FREE VOLUME MEASUREMENT

Besides the surface area, pore size is another important consideration in the study of catalysts.

For given catalytic reactions, the pore size of the catalyst must be large enough for the reactants which can diffuse freely into the pore and then adsorb at the active sites on the surface of the pore. If the reactants are high-boiling point organic compounds, such as heavy or residual oil, large pores are required. It was suggested that a pore size distribution between 100 to 150 Å is suitable for reforming processes.

The method for measuring pore size is the Mercury Porosimeter, which was first suggested by Washburn[47] and developed by Ritter and Drake.[48,49] The porous solid was placed in a long-neck sample tube, and the entire dilatometer was then filled with mercury and placed in a protective bomb to which nitrogen pressure up to 60,000 psi could be applied, mercury penetrated increasingly into the pores of solid, and an increasing length of resistance wire was exposed in the neck of the dilatometer; by measuring the resistance of the wire, the volume penetrated could then be calculated, based on the following equation:[47]

$$D = \frac{-4\sigma\cos\alpha}{P}$$

where D is the diameter of the pore just enterable by mercury with surface tension σ, under pressure P and at a contact angle α with the material being tested.

Mercury porosimeter method is, of course, not available for measuring closed pores. It is not available for determining the hidden pores either, due to the "ink bottle" effect.[50]

PASCA technique has shown its powerful capacity in estimating pore size of both closed pores and open (including hidden) pores. When the experimental values of positron lifetimes in several porous materials reported by Perkal and Waiters,[51] Ito et al.,[52] Chuang and Tao,[53] and Hsu et al.[54] were plotted as a function of mean pore radius in Figure 6,[55] a good correlation between the mean pore radius and the lifetime corresponding to the o-Ps annihilation in the pores was found.[55]

It is widely known that calcination temperature has a strong effect on the surface area, the pore size of a catalyst and the dispersion of the metallic component at surface of a catalyst, and consequently has an effect on the activity of the catalyst. Young[56] reported the calcination temperature for the Co-Mo/zeolite hydrocracking catalyst is 482°C. Our preliminary investigation of ammonium molybdate on calcination temperature by PASCA shows that the highest o-Ps lifetime is located at about 480°C (see Figure 7).[57] This is not surprising because the highest lifetime of o-Ps is correlated with the highest porosity of the molybdenum oxide, MoO_3. Obviously, when calcinating at 480°C, MoO_3 has the highest degree of dispersion at the surface of Co-Mo/zeolite catalyst. Our results provide a simple and powerful way to correlate the activity of a heterogeneous catalyst with the porosity of its individual metallic component. Due to the very small size of pores (super-micro pores) and very small surface area in this kind of material (such as MoO_3), it can be measured neither by BET nor by mercury porosimeter.

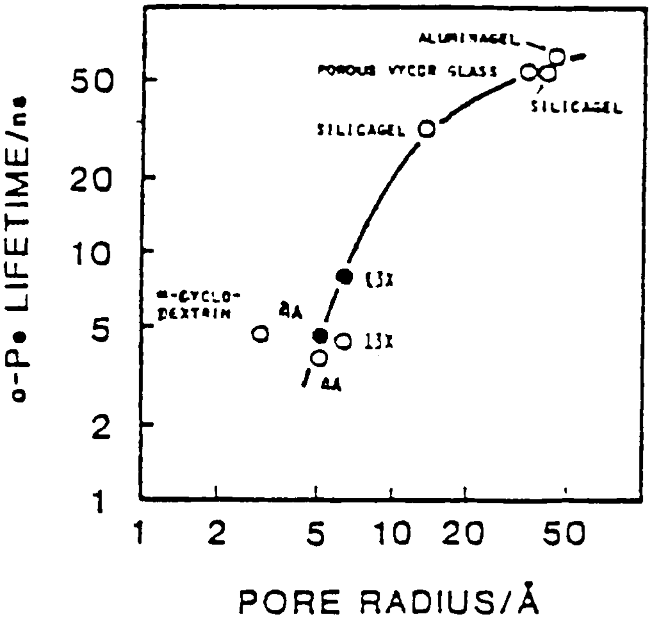

FIGURE 6. Correlation between pore size and o-Ps lifetime.

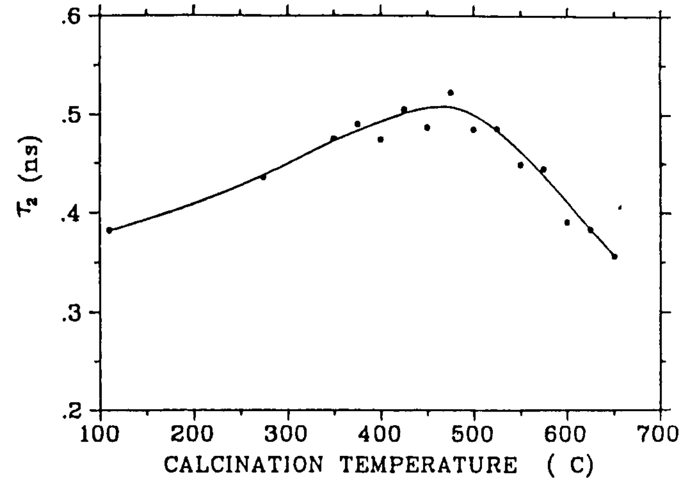

FIGURE 7. Correlation between calcination temperature and τ_2 value.

PASCA has also been applied to investigate free volume of polymers. According to the "free-volume theory",[59] the rate of positron or Ps annihilation, in the absence of chemical reactions or spin conversion between Ps and matter, is a function of the effective free volume. The increase of dimension of the free-volume sites results in an increase of the Ps lifetime. For simple van der Waals bonded molecules, the free volume and the observed o-Ps lifetime fall onto a universal curve (see Figure 8).[60]

The free volume theory has been applied to study teflon and polyethylene.[61] The PASCA study of epoxy polymers by Y. C. Jean et al.[58] has found that the free volumes for four

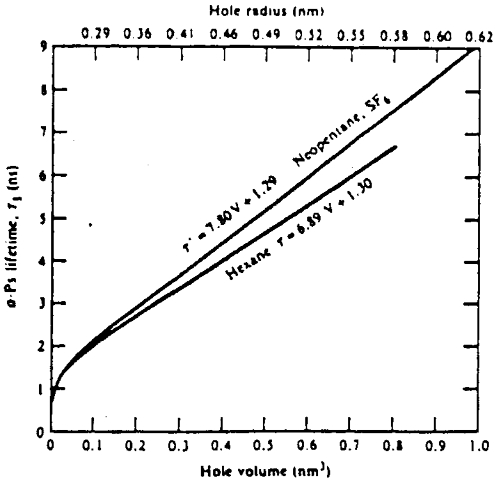

FIGURE 8. Correlations between o-Ps lifetime and free volume in molecular substrates.

epoxies with different crosslinking vary almost 10 times (from 0.025 to 0.220 nm^3) over the temperature range between −78 and 250°C.

VIII. ANALYSIS OF BULK MATERIALS

When a positron enters into the condensed matter, it is thermalized and may annihilate in the bulk, resulting in a τ_1 (λ_1) and I_1. Both peroxide and active chlorine are Ps scavengers. The I_1 is a proportional to the bulk content of peroxide and active chlorine. A simple quantitative positron annihilation method for determining potassium peroxymonosulfate and calcium hypochlorite in bleaching powder has been developed.[29] This is a non-destructive method. It is noted that we will use I_1 to obtain the bulk information, instead of τ_3 or I_3 for the surface information. The unknown may be easily determined when a calibration curve is prepared:

$$I_b = I_b^o + K_b[M]_b$$

where subscript b denotes the bulk.

Dlubek and Brummer recently reported the use of positron as a probe for the bulk and defect of semiconductors.[20]

IX. DEFECT CHARACTERIZATION

Study of vacancy formation in metals has been actively pursued for more than 20 years using differential dilatometry, quenching, and more recently, positron annihilation spectroscopy. One of the early important applications of positron annihilation to the condensed matter was the detection of defects in metals. Significant contributions have been primarily in two aspects: (1) the characterization of atomic defect properties, particularly those monovacancies, and (2) the determination and understanding of vacancy-like microstructure developed during irradiation and annealing. The study of defects in metals by positron annihilation spectroscopy has been reviewed by Siegel[7] and by Gauster.[30] Numerous papers on defects in solids can be found in literature. They have focused on the investigation of vacancy formation, vacancy migration and vacancy clustering in metals. A special chapter was devoted to this subject.[75]

Dislocation and grain boundaries in metals have been recognized as traps for positrons, and many studies have been reported.[31] Zhou et al.[32] have studied the positron trapping at grain boundaries showing a fairly linear relationship by plotting the positron mean lifetime ($\bar{\tau}$) as a function of $1/\mu$ (μ = grain size) in the Zn-22 wt% Al alloys.

Crystallinity is an important factor which makes zeolites much more active and selective than amorphous materials.[62] The presence of some defects in zeolites will reduce the crystallinity and hence reduce the activity, particularly the selectivity. By using high resolution electron microscope, two types of defects related to sodalite and offretite zeolites, which can affect the catalytic and sorptive properties of the parent zeolites, have been identified.[63] In study of the faujasite zeolites using PASCA, an unusual high lifetime component (about 50 ns) was found, which was supposed to be a kind of defect in the zeolites.[55] PASCA presents an alternative method for determining defects in zeolites.

X. STUDIES OF CHEMISORBED GASES ON POROUS MATERIALS

By using the lifetime measurement, the chemical reactivities of NO_2, SO_2, NO, and O_2 in porous media have been studied.[33] The long-lived component ($\tau_2 \sim 5$ ns, and $\tau_3 > 30$ ns) are attributed to positron annihilation on the surfaces and in the microvoids of the porous media. The observed chemical reactivities between Ps atoms and gas molecules in the microvoids are found to be smaller than those reported for free gases due to caging effect. Chemical reactivities on the surfaces between the Ps and the chemisorbed gas molecules, which are in anionic states, are higher than those in the microvoids. The chemical reaction rate constant (K) may be calculated according to the following equations:

$$\lambda_v = \lambda_v^o + K_v[M]_v$$

$$\lambda_s = \lambda_s^o + K_s[M]_s$$

where subscripts v, s, are o-Ps annihilation rate in void and on surface, respectively. [M] is the moles of adsorbed gas per m^2 of the adsorbent. In Figure 9,[34] a linear relationship between

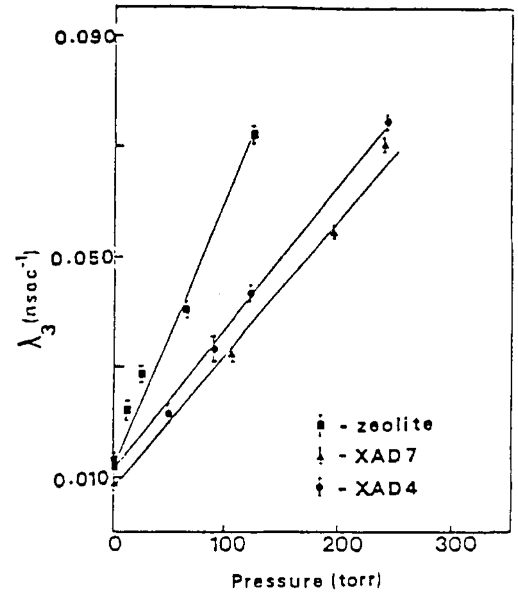

FIGURE 9. Ps annihilation rate in the void vs. equilibrium pressure of NO_2 in different materials.

the λ_3 and gas pressure exists. In Figure 10,[35] the curve for zeolite Y is not straight; two linear lines intersect at certain ΔP value. It seems that the zeolite Y curve indicates two Ps annihilation rates with two different slopes. At the beginning, the rate is faster; after the surface has been covered by the gas molecules, its Ps annihilation rate decreases. It is clear that the Ps annihilation rates are a function of the gas molecules chemisorbed at the surfaces.

The PASCA study has shown that there is a significant difference between the adsorption of SO_2 on τ-alumina and on Ni/τ-alumina catalyst.[69] On neat γ-alumina (surface area = 100 m^2 and calcined at 450°C), λ, the o-Ps reaction rate starts increasing at Δ P about 120 torr, which is related to 32% of the surface area covered by SO_2 and which indicates that the active sites for SO_2 gas adsorption occupy 32% of surface area of the alumina. In the NI/τ-alumina catalyst (4 wt% Ni and calcined at 450°C), the number of active sites increases up to 80% of the surface area, which is 2.5 times as the adsorption capacity for the pure γ-alumina (see Figure 11).[69] This is understandable that Ni- or Co-containing catalysts, in general, are for desulfurization or hydrodesulfurization reactions.[70,71] The results indicate that it is possible to use PASCA and gas (such as NO_2, SO_2, Cl_2, NH_3, pyridine, etc.) adsorption technique to study some special catalytic reactivities.

XI. DETERMINATION OF Ps INHIBITORS

Talamoni et al.[36] have shown that in polar solvents, some solutes lead to a limited inhibition of Ps formation (halides, Co^{2+}, Ag^+, H^+), while with others (NO_3^-, $Te(OH_6)$), there is a complete inhibition at a sufficiently high concentration. They studied the effects of temperature on the Ps formation and inhibition in liquid using ethyleneglycol as solvent and found that the first class promoted inhibition which is strongly temperature dependent in contrast to the second class.

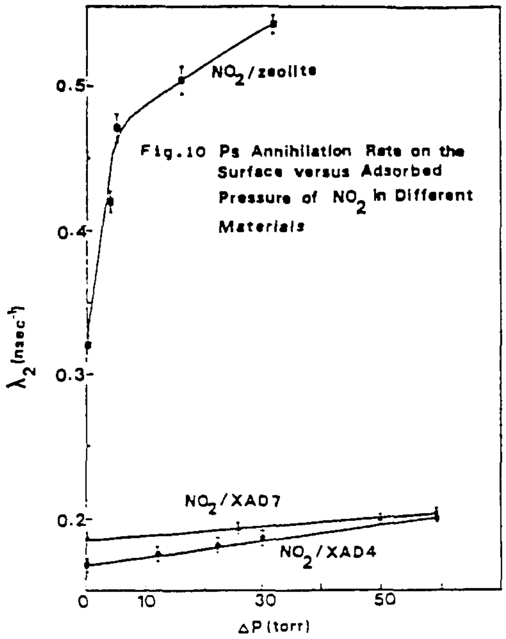

FIGURE 10. Ps annihilation rate on the surface vs. adsorbed pressure of NO_2 in different materials.

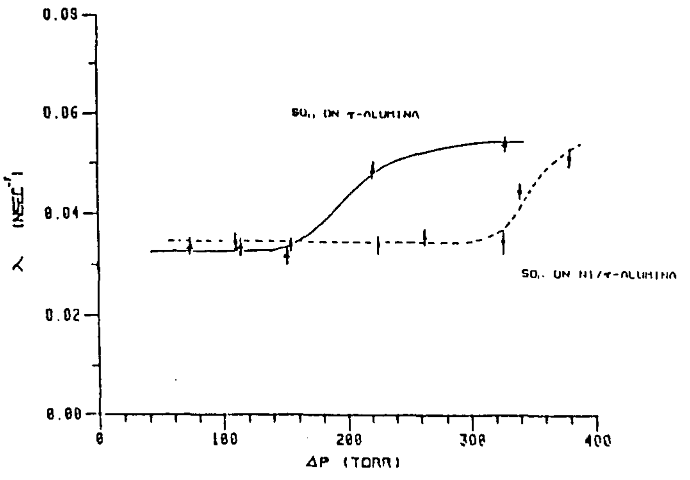

FIGURE 11. Difference of SO_2 adsorption between γ-alumina and Ni/τ-alumina catalyst.

The variations of I_3 for Cl^- and ClO_4^- ions or $1/I_3$ for NO_3^- ions show correlations at temperatures of 294, 356, and 413 K. Figure 12[36] presents linear relationships of nitrate concentration vs. $1/I_3$.

In the plots for Cl^- and ClO_4^-, there is a sharp decrease in I_3 (%) vs. Cl^- or ClO_4^- ion concentration in ethyleneglycol. It is feasible to utilize the quantitative relationship about the inhibition of Ps formation for the determination of these ions.

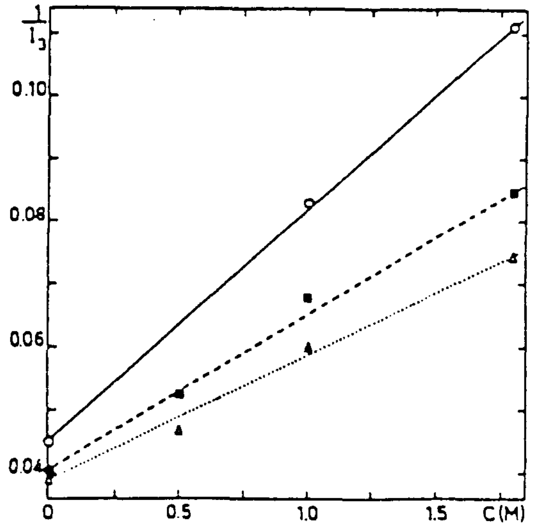

FIGURE 12. Variations of $1/I_3(\%)^{-1}$ with concentration C of NO_3^- at ○, 294 K; ■, 356 K; △, 413 K.

It was noted that in other solvents, Cl^- leads to a limited inhibition, while I_3 indicates nothing with increasing nitrate concentration. ClO_4^- appears to belong to the same class of solutes as Cl^- with a rather good inhibiting power compared to its low efficiency in water. It seems that the strong electronegative elements combining with oxygen tend to effectively inhibit the Ps formation. By selecting a proper solvent, quantitative procedures for determining these anions based on the changes in $1/I_3$ may be established.

Unlike in water or ethyleneglycol solution, NO_3^- ions show a limited inhibition on surface of γ-alumina and γ-alumina based catalysts.[68]

Wikander[37] has studied a number of compounds as Ps inhibitors in non-polar solvents.

XII. POSITRON ANNIHILATION USED IN TLC

A system for the determination of spacial distribution of organic molecules labelled with positron emitting radionucleides on thin layer chromatography (TLC) plates has been described.[38] Isotope ^{18}F and a mixture of different iodine isotopes are used in the spot testing in the TLC plates.

The system employs an inexpensive plastic scintillator, standard nuclear electronics and computer hardware and software commonly available in a research laboratory working with positron emitters. A schematic diagram of detection system is known in Figure 13.[38]

The use of ^{18}F isotope shows more sensitive TLC than that of ^{123}I, ^{124}I, and ^{130}I. The system for measuring radionucleides on TLC demonstrated to be a useful tool in work with positron-emitting radionucleides. It combines the advantages of good resolution, sensitivity, and accuracy together that one would expect with TLC. Figure 14[38] shows a scan and an autoradiogram of an undeveloped TLC strip with spots of ^{18}F.

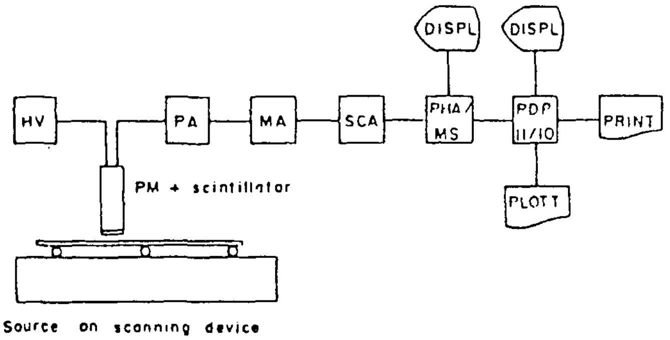

FIGURE 13. Schematic diagram of detection system. HV = high voltage; PA = pre-amplifier; MA = main amplifier; SCA = single channel analyzer; PHA/MS = pulse height analyzer in the multiscaling mode; PDP 11/10 = computer.

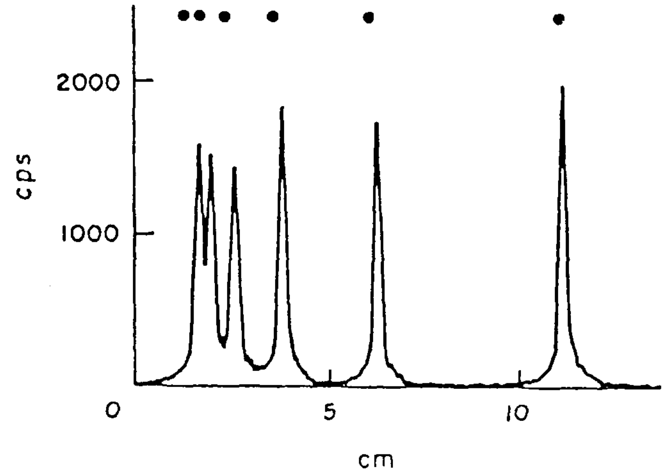

FIGURE 14. Test chromatogram and autoradiogram of ^{18}F; text.

XIII. DETERMINATION OF IMPURITIES

A systematic study by Goworek and his collaborators on the effect of impurities and temperature on the positron annihilation pointed out the possibilities of determining impurities.[39] In the crystals of p-terphenyl and pyrene at room temperature, neither a long lifetime nor a narrow component is found. However, on doping p-terphenyl with various organic impurities, both In and I_2 show a sigmoidal increase with the impurity concentration as illustrated in Figure 15.[39]

Trane and Evans[40] reported the lifetime changes associated with the argon annealing. The argon contained 200 ppm of N_2, 3 to 5 ppm of O_2, and 5 to 7 ppm of CO_2. They concluded that the impurity effects were responsible for the increased values of τ_2 in voids of molybdenum.

Positron annihilation in pure solids generally yields two lifetime components: a short lifetime in the order of 10^{-10} s is due to the annihilation from the free state and the bound

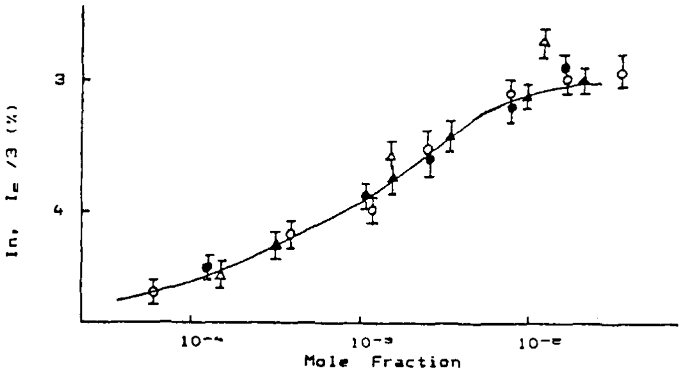

FIGURE 15. Intensities of the I_e (close signs) and the narrow component In (open signs) in p-terphenyl vs. mole fraction of impurities. Circles are for anthracene, triangles for 2,3-benzofluorene.

state of singlet p-Ps; and a longer lifetime component in the order of 10^{-9} s is attributed to the annihilation of the triplet o-Ps into two photons by a pickoff process. The intensity of this latter component, which is a measure of degree of the overlap of positron-lattice electron wave function, depends on, among other factors, the lattice disorder caused by impurities. Hsu et al.[41] studied the positron lifetime spectra of pure (99.999%) and less pure quality of phenanthrene, and found that the intensity of the longer-lived component, I_2, is larger for the pure sample (see Figure 16).[41]

XIV. STUDY OF ADSORPTION AND DESORPTION OF CATALYSTS

Three lifetime components in a series of metal ion impregnated zeolites, M-Nay (M = Li, Fe, Cr, Cu, etc.) have been studied.[42] The chemical states in the voids and on the surface may be characterized by positron annihilation technique. In these metal zeolites, the Ps enhancement as a function of concentration of adsorbed ions was observed. The best fitted anti-inhibition constants, K, follows an equation:

$$I_3 = I_3^o + K[M]_s$$

where $[M]_s$ = mole fraction of metal ion per kg of zeolite, I_3^o and I_3 are the intensity of surface Ps state in the neat zeolite Y and in the impregnated zeolite Y, respectively.

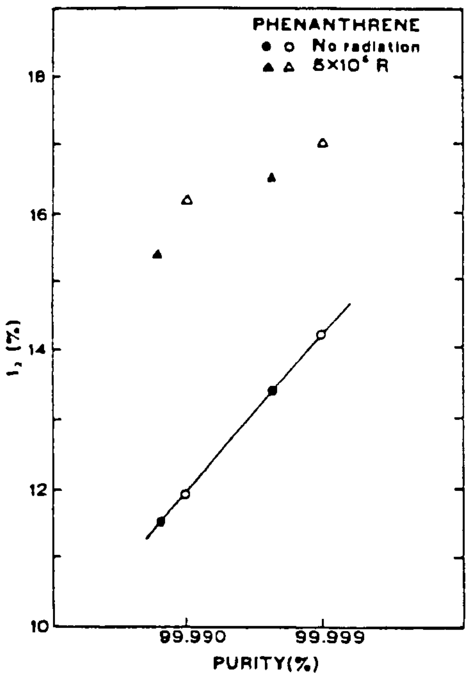

FIGURE 16. Variations of I_2 in phenanthrene: open circles are Princeton Organics sample before irradiation, open triangles after 5 × 10^6 R irradiation; closed circles are Eastman sample (purity estimated) before irradiation, closed triangles after 5 × 10^6 R irradiation.

It was suggested that the metal ions adsorbed on the zeolite surface might behave as deep traps for electrons, which may be excited from the valance band to the conduction band. There may exist relationships between the catalytic activity of transition metal ion adsorbed on the zeolite surface, the acidity or basicity of surface, and the polarization power of the cations. A quantitative approach to evaluate such important properties of a catalyst has been studied.[42] A concentration dependence study of M-NaY (M = Li^+, Cs^+, Cu^{2+}, Ni^{2+}, Fe^{3+}, Cr^{3+}, Zr^{4+}, and Th^{4+}) was carried out at room temperature by the PASCA technique. Figures 17 and 18[42] show the linear relationships between I_s (%) and I_2 and metal ion concentrations of copper and nickel. Different metal ions on the zeolite surface exhibit different slopes. The Th^{4+}, different from Zr^{4+}, showed little effect on the intensity or the annihilation constant.

Figure 19[42] shows a plot of the Bronsted acidity, and the charge to radius ratio vs. log K. The correlation between charge to radius ratio of the metal ions and the log K is linear except for the Cu^{2+}, Fe^{3+}, and Li^+ ions. The excellent quantitative correlation between log K and Bronsted acidity provides a novel and a unique methodology to study the nature of surfaces, the acidity and basicity of surface active sites, catalyst poisoning, as well as its efficiency.

PASCA technique has also been applied to study catalytic reactions on γ-alumina surfaces as a function of impregnated metal ion concentration.[43] Ps inhibitions were observed due to the presence of metallic nitrates. Figure 20 shows the corre-

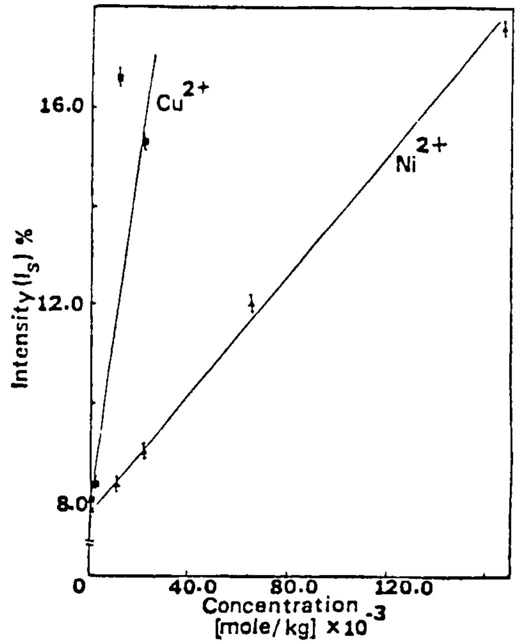

FIGURE 17. Adsorption of Ni^{e+} and Cu^{e+} on zeolit Y vs. I_s.

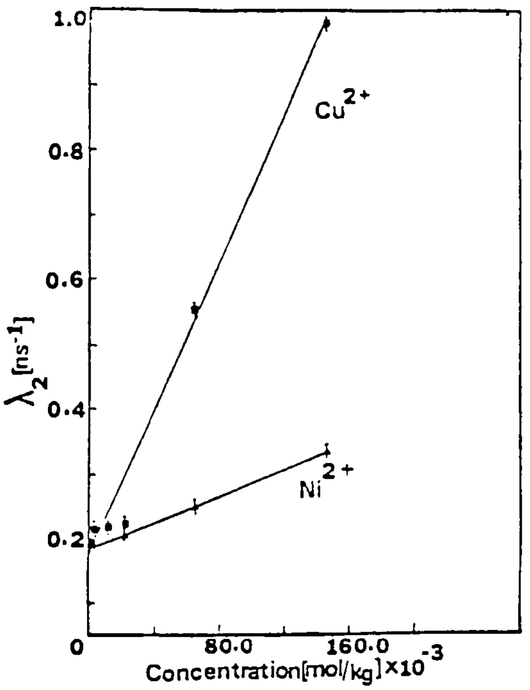

FIGURE 18. Adsorption of Ni^{2+} and Cu^{2+} on zeolite Y vs. λ_e.

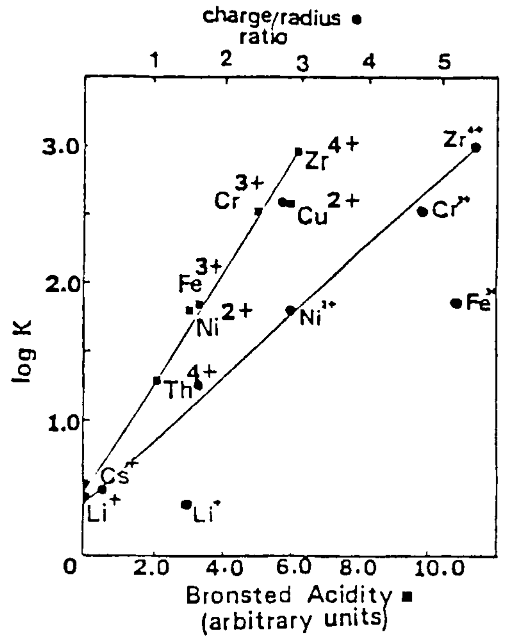

FIGURE 19. Bronsted acidity vs. log K.

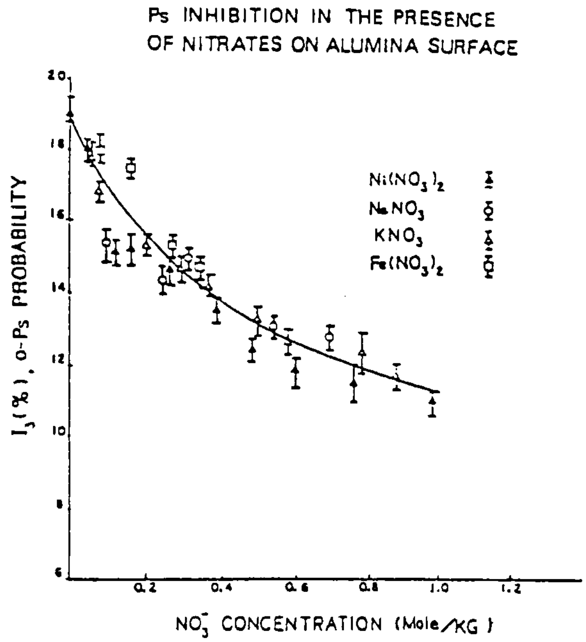

FIGURE 20. Correlation between I_3 and metallic nitrate concentration.

lation between I_3 and nitrate concentration, C, which was fitted into the following equation:

$$I_3 = I_3^0(1/(1 + KC) + 1 - f)$$

where f = fraction of Ps liable to limited inhibition, K = inhibition constant, and C = concentration. Figure 21 shows a linear relationship between the f value and the oxidation states. In this case, the increase of f value may be attributed to the increase of the positive charge of metal ions in the nitrates.

XV. IDENTIFICATION OF OXIDATION STATES

There are not many *in situ* analytical techniques available to determine oxidation states. The significant one is the X-ray

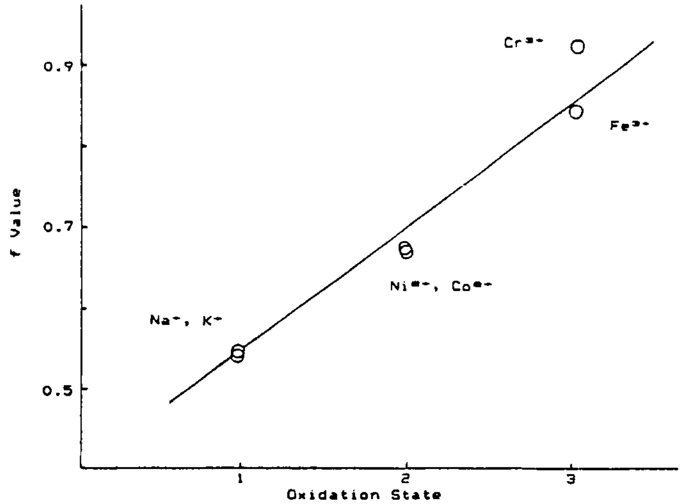

FIGURE 21. Relationship between f value and the oxidation state.

photoelectron spectroscopy (XPS or ESCA) which has certain limitations. Our preliminary results are encouraging in that the PASCA may provide an analytical technique to identify the oxidation states (see Figure 22).[44] Sodium halogenides (NaF, NaCl, NaBr, and NaI) have two lifetime components; for comparison we used mean lifetime ($\tau = \tau_1 \times I_1 + \tau_2 \times I_2$), while the other compounds have only one component. The λ value and the oxidation states of halogens show roughly a linear correlation except $NaClO_4$ which has a lower λ value than expected. This is probably due to the steric effect that the ClO_4^- ion has a tetrahedral configuration, instead of the pyramidal structure for ClO_3^-, in which the Cl atom is located in the center and surrounded so tightly by four oxygens that the hot positron is difficult to penetrate to the center atom, Cl.[45]

The results shown in Figure 22 are interesting. Further work along this line should be explored.

XVI. TO DISTINGUISH STERIC STRUCTURES

It has been mentioned previously that the $NaClO_4$ has lower value than expected due to its special steric structure.[45]

In fact, the steric effect strongly affects the reactivity between o-Ps and substance. Studies of a series of nitrobenzene derivatives in benzene solution have shown[64-67] that nitroaromatics have much higher reaction rate constants than nitro aliphatics because the $-NO_2$ functional group in aromatic molecule is coplanar with the big conjugation system, in which π-electrons move from the benzene ring to $-NO_2$ functional group, and consequently, both of the oxygen atoms in the $-NO_2$ group have "excess" of electron (see Figure 23).[67]

It has also been proved[64-47] that the existence of bulky substituents in ortho position of nitroaromatics causes the rotating of the nitro groups out of the aromatic plane and hence inhibits the positronium reaction rate dramatically (see Figure 24).[67]

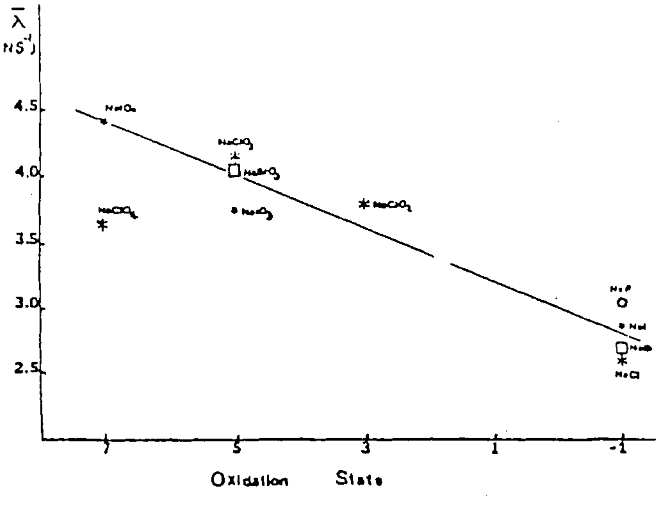

FIGURE 22. Relationship between reaction rate (λ) and oxidation state.

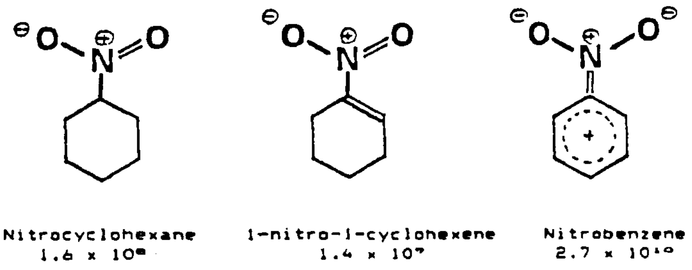

FIGURE 23. Correlation between the molecular structure and o-Ps reaction rate constant.

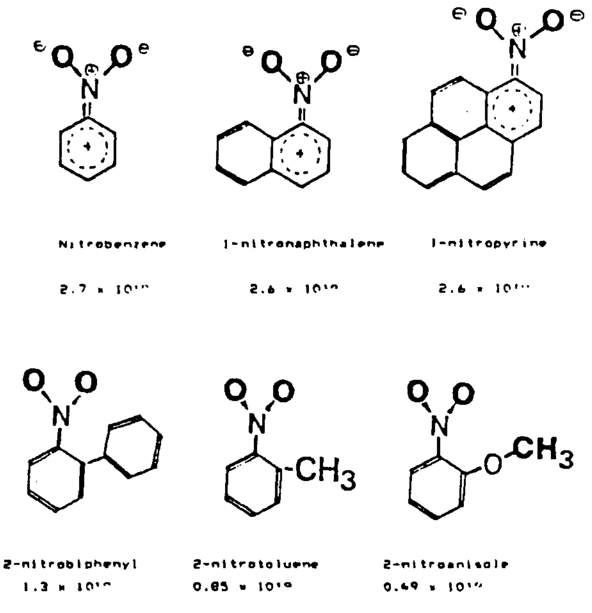

FIGURE 24. The steric effect on the o-Ps reaction rate constant (K) by introducing different substituents in ortho position of the nitro group. 1-Nitronaphthalene can be considered as a daughter benzene ring connecting to the mother ring either in the ortho and in the meta positions; 1-nitropyrene can be treated as a daughter phenalene ring connecting to the benzene ring in three positions (ortho, meta, and para).

The steric effect may be used to distinguish the structural difference between aliphatic and aromatic nitro compounds or between ortho- and para- or meta-nitroaromatics.

XVII. PREPARATION OF SAMPLES FOR MICRO QUANTITIES

In dealing with micro quantity samples, the sample may be adsorbed by a porous resin prior to the lifetime measurements. The results in Figure 25 were obtained after adsorption of the chloro-phenols on the XAD-2 resins, which indicates the quantitative linear correlation between the reaction rate on the surface (λ_3) and concentration. Another way for microanalysis is to dissolve the sample into a solvent and then measure

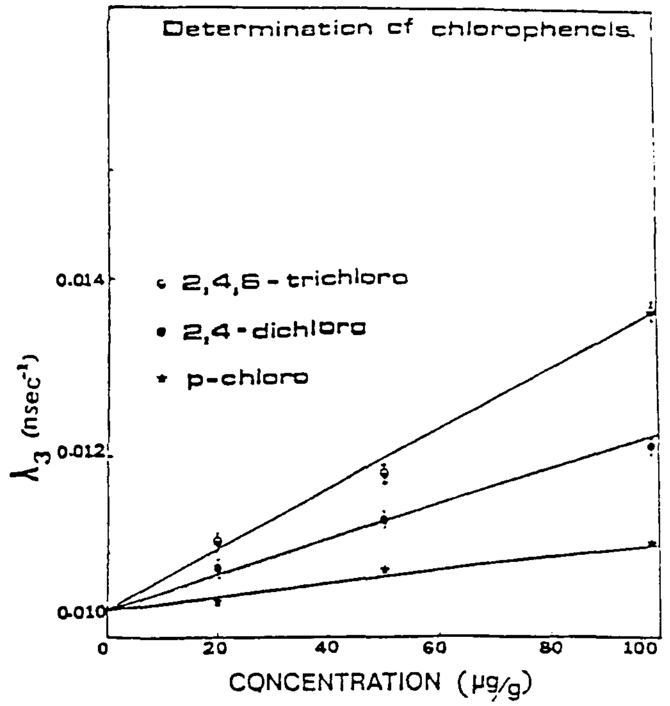

FIGURE 25. Determination of chlorophenols.

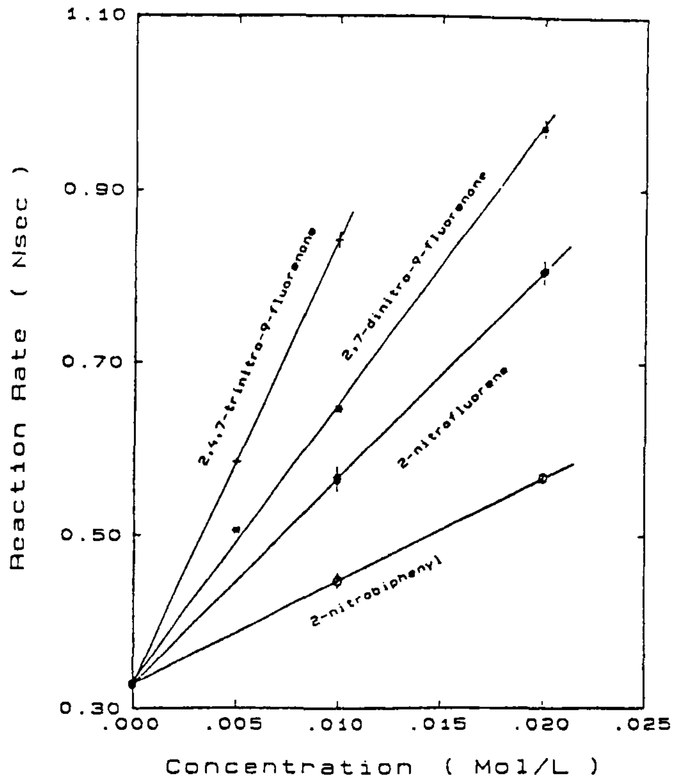

FIGURE 26. Quantitative correlation between the concentration of nitroaromatic and ortho-positronium reaction rate.

the lifetime spectrum of the solution. The sensitive and quantitative examples are the determinations of nitro organic compounds, for example nitrobenzene in benzene solution, etc.[64-67] For determining nitroaromatics, PASCA technique can detect as low as 0.02 wt% (in N). There is a very good quantitative correlation between the reaction rate (λ_3) and the concentration of nitroaromatic (see Figure 26).[67]

XVIII. POSITRON ANNIHILATION METHOD WITH ION BEAM ACTIVATION

Lifetimes of the positron emitting nuclides formed during the positive ion irradiation differ over a wide range. If the analytical detection system is capable of measuring lifetimes down to a few seconds, many elements can be analyzed by the positron annihilation method with ion beam activation, particularly among the lighter elements. The measurement of the positron annihilation at high levels of activity, due to a number of simultaneously activated nuclides, presents problems of a technical nature. On account of the specificity and sensitivity inherent in the ion beam activation technique, the positron annihilation as a quantitative technique with ion beam activation has been developed. For details, the readers are referred to Sellschop et al.[46]

In photon or neutron activation analysis, the problem of rapid transfer following irradiation is accomplished by irradiation in air. For ion beam activation, the beam exposure must be in vacuum. Sellschop et al.[46] designed a system that transfers irradiated samples rapidly from the high vacuum region. Although the ion beam technique is *ex situ*, it is particularly useful for the lighter elements which are generally not amenable to neutron activation analysis. It is quantitative and non-destructive, and able to provide information about profiles of impurities.

In geological and metallurgical samples, seldom fewer than two positron decays are activated, and sometimes as many as four. Judicious selection of irradiation times and decays at onset of counting can eliminate some of the interesting activities. For an undesired activity that has a halftime within a factor of 3 or 4 of the activity of interest, it is then necessary that the decay spectra should be carefully deconvoluted. They developed a NIND computer program for this purpose.

It has been routinely used as a quantitative method with ppm sensitivity. Table 3 shows some examples of positron analysis used in various samples. C, N, O, Na, Al, and Ca in a variety of matrices have been determined.

XIX. POSITRON-EMITTING ISOTOPE AS A TRACER

One of the most powerful tools for nuclear medicine's research is Positron emission tomography (PETT), which gives clinicians and researchers a non-destructive means of probing the biochemical processes of the body from the outside. In a

Table 3
Some Samples Analyzed by Positron Annihilation Ion Beam Activation

	Reaction	Samples	Half-life
1.	Proton-induced		
	(a) $^{12}C(p,\gamma)^{13}N$	Minerals	10.0 min
	(b) $^{13}C(p,n)^{13}N$	Various	10.0 min
	(c) $^{14}N(p,n)^{14}O$	Various	71.0 s
	(d) $^{16}O(p,\alpha)^{13}N$	Various	10.0 min
	(e) $^{17}O(p,\alpha)^{18}F$	Various, coal	109.7 min
2.	^{3}He-induced:		
	(a) $^{12}C(^{3}He,\alpha)^{11}C$	Various	20.3 min
	(b) $^{12}C(^{3}He,n)^{14}O$	Various	71.0 s
	(c) $^{16}O(^{3}He,p)^{18}F$	Diamond, coal, metals	109.7 min
3.	α-induced:		
	(a) $^{12}C(\alpha,n)^{15}O$	Various	124 s
	(b) $^{14}N(\alpha,n)^{17}F$	Diamond	66 s
	(c) $^{23}Na(\alpha,n)^{26m}Al$	Metals	6.4 s
	(d) $^{27}A(\alpha,n)^{30}P$	Coal	2.58 min
	(e) $^{40}Ca(\alpha,p)^{43}Sc$	Coal	3.79 h
4.	Heavy ion induced		
	(a) $^{12}C(^{12}C,d)^{22}Na$	Various	2.6 y

PETT experiment, the subject is injected with radiochemical labeled by a positron emitter, the most common used being ^{11}C, ^{13}N, ^{15}O, and ^{18}F. The positrons emitted by these atoms travel only a few millimeters through the surrounding tissues before annihilating into two γ-rays, which are monitored by an array of NaI scintillation counters. The advantages offered by PETT are that it allows the research on live animals and in humans. The radiopharmaceutics could be made that were physiologically identical to the body's own compounds. Because of the short life of the isotopes, a small cyclotron plays a central role in PETT research.

Many biochemicals may be synthesized on the spot and the experiments are carried out without much delay.

XX. ENVIRONMENTAL MOLECULES

By employing the lifetime technique the chemical reactivities of NO_2, SO_2, NO, and O_2, Ni^{2+}, Cu^{2+}, Co^{2+}, and other ions in porous media have been studied.[76] Two long-lived components ($\tau_2 \sim 5$ ns, $\tau_3 > 30$ ns) have been attributed to positron annihilation on surface and in the microvoids of the media. The observed chemical reactivities between positronium atoms and gas molecules in microvoids are found to be smaller than those reported for free gases due to caging effect. The reactivities on the surface between Ps and adsorbed molecules (anionic formed) on the surface are found higher than those in the microvoids.

XXI. STUDIES OF OIL SHALES

The positron lifetime and intensity of Green River oil shales as a function of temperature have been measured by PASCA. The long-lived o-Ps lifetime (~1.3 ns) indicates that the shale structure consists of interfacial spaces. The quantitative fraction of these layer spaces equal to 4% as measured by o-Ps component. The decomposition of internal organic compounds takes place at 350°C. The decomposition continues up to the temperature about 450°C. Above 450°C, the shale structure becomes void-like since all organic molecules have escaped. The void concentration increases from 5% to 20% as the temperature increases from 450 to 600°C as measured by o-Ps intensity. However, the void size decreases as a function of temperature.[76]

XXII. SUPERCONDUCTORS

Positron annihilation has been applied to study the superconductors. Stump and Talley[79] indicated larger value of the mean lifetime in the superconducting state than in the normal state. Tripapathy and Bhuyan[80] evaluated the mean lifetime of positron in superconducting Al was $\sim 10^{-5}$ s compared to its value of $\sim 10^{-9}$ s obtained for the normal state. The annihilation rate increases slowly as the temperature of the system varies from $T = O$ to $T = T_c$.

Hatano et al. studied the charge density wave phase transition in 2H-$NbSe_2$ at temperature 32 K by positron annihilation.[81] A large anisotropy was found in electron momentum distribution in this low dimensional conductor at 298 K. The anisotropy was decreased in the momentum distribution curve observed along layers at 25 K. The authors claimed it is a clear evidence of the disappearance of the Fermi surface due to charge density phase transition at 32 K.

The high temperature superconductors have recently been reported. Jean et al.[82] have studied the high temperature superconductors, $YBa_2Cu_3O_{6+}$, by PASCA as a function of temperature between 10 to 293 K. They observed the positron lifetime and Doppler broadening S-parameter increased near the superconducting critical temperature, $T_c = 90$ K. The nonconducting sample containing a similar structure with high oxygen vacancy content did not show such a change. These results give evidence that the oxygen vacancy and electronic structure change play an important role for high temperature T_c superconductivity.

XXIII. CARBON FIBERS, EPOXY POLYMERS, AND CARBON EPOXY COMPOSITES

The fiber fractions found by PASCA is related to the apparent volume fractions determined by density measurements. Positron annihilation centers have been found that appear to have been created at the carbon epoxy interface when the composite was prepared. Characterization of this interface is important for the development of composites with improved mechanical properties.[83] Free-volume properties of polymers,

Table 4
Selected Positron Sources

Isotope	Half-life	Means of production	End-point Energy(MeV)
^{22}Na	2.67 y	$^{55}Mg(p,\alpha)^{22}Na$	0.54
^{68}Zn	245 d	$^{64}2n(n,\tau)^{65}Zn$	0.33
^{64}Cu	12.8 h	$^{63}Cu(n,\tau)^{64}Cu$	0.66
^{58}Co	71 d	$^{58}Ni(n,p)^{58}Co$, $^{55}Mn(\alpha,n)^{58}Co$	0.48
^{55}Co	18.2 h	$^{58}Ni(p,\alpha)^{55}Co$, $^{54}Fe(p,2n)^{55}Co$	1.50
$^{68}Ge/^{68}Ga$	275 d	$^{66}Zn(\alpha,2n)^{68}Ge \xrightarrow{275d} {}^{68}Ga$	1.88 1.90
^{57}Ni	36 h	$^{54}Fe(^{3}He,2n)^{57}Ni$	0.85
^{90}Nb	14.7 h	$^{90}Zr(p,n)^{90}Nb$, $^{90}Zr(d,2n)^{90}Nb$	1.50
^{44}Ti	4.8 y	$^{45}Sc(p,2n)^{44}Ti \xrightarrow{4.7\gamma} {}^{44}Sc$	1.47
^{11}C	20.3 m	$^{12}C(^{3}He,\alpha)^{11}C$	0.98
^{13}N	10.0 m	$^{12}C(p,n)^{13}N$	1.19
^{18}F	109.7 m	$^{17}O(p,\alpha)^{18}F$	0.635

such as hole sizes, contents, and structure have been determined by PASCA.[58,84]

XXIV. ADVANTAGES AND LIMITATIONS OF PASCA TECHNIQUE

Any analytical technique, which can exist, must have its advantages. Meantime, no technique can do everything; it must also have its limitations. The advantages and limitations of PASCA may be listed in the following.

Advantages:

1. It is non-destructive.
2. It is *in situ*.
3. It is capable of probing the hidden surfaces.
4. It provides a new method to determine surface area.
5. It can work in vacuum, as well as at high pressure.
6. It can work at both high and low temperature.
7. It has good resolution.
8. It is quantitative, and better than other techniques.
9. It is a method for both bulk and surface information.
10. It is sensitive to electronegative elements.
11. It has potential for oxidation states.
12. Easy sample preparation.
13. For microanalysis.
14. For gas, liquid, and solid state samples.
15. It can be used to study micellar systems.
16. It can determine formation constants in systems where the other spectroscopic measurements are difficult.
17. It can study voids and free-volumes.
18. It provides a new method for study of the defects in zeolites.
19. It is capable of distinguishing some steric structure.
20. It has a special sensitivity to probe high T_c superconductivity.

Limitations:

1. Reaction mechanisms are not yet quite clear.
2. Sometimes data analysis is still not conclusive.
3. Requires better fast scintillation counters with short time resolution and high efficiency.
4. It is not sensitive to all elements.
5. It is not for qualitative identification of elements or compounds in many cases.
6. Usually sensitivity not below ppm levels.
7. Instrumental adoption may require simpler form in order to be used as a routine tool.
8. The Doppler broadening energy spectra is not stable and simpler to operate.
9. Factors such as excitation of molecular vibrational and rotational modes and the formation of positron molecular complexes may contribute to the observed signals.
10. A compact, easy working, commercial instrument is lacking.
11. Dealing with radioactivity, subject to certain safety restrictions.

XXV. CONCLUSION

From the experimental results which have been presented, it is clear that the PASCA is a quantitative technique, particularly useful for the surface studies. It is a non-destructive and *in situ* method. It can be used for determining both the bulk and surface concentration even at ppm ranges. It possesses the potential for the identification of oxidation states based on the lifetime information. It is capable of distinguishing steric structures for some organic compounds. Quantitative applications of the catalytic studies (zeolites and γ-alumina) have been demonstrated. It also provides unusual information about the properties of porous materials, such as surface area, hidden surface, surface acidity, surface profile, defects, interfacial grain boundary, dislocation, pollutants, impurities, etc. The application area may include metallurgy, biochemistry, electrochemistry, colloid and surface science, semiconductors and superconductors, etc. Present results have built enough solid foundation for further advances.

ACKNOWLEDGMENT

The authors wish to thank Tariq Mahmood for his assistance in preparing the manuscript.

REFERENCES

1. **Dirac, P. A. M.,** *Proc. Camb. Phil. Soc.*, 26, 361, 1930.
2. **Anderson, C. D.,** *Phys. Rev.*, 41, 405, 1932.
3. **Anderson, C. D.,** *Phys. Rev.*, 43, 491, 1933.
4. **Anderson, C. D.,** *Phys. Rev.*, 44, 406, 1933.
5. **Deutsch, M.,** *Phys. Rev.*, 82, 455. 1951.

6. **Deutsch, M.,** *Phys. Rev.*, 83, 866, 1951.
7. **Siegel, R. W.,** *J. Madras Univ. Section B*, 45, 1, 1982.
8. **Alam, A. and West, R. N.,** *J. Madras Univ. Section B*, 45, 38, 1982.
9. **Nieminen, R. M.,** *Positron Annihilation*, Jain, P. C., Singru, R. M., and Gopinathan, K. P., Eds., World Science Publishing Company, Singapore, 1985, 437.
10. **Ache, H. J.,** *Positronium and Muonium Chemistry*, Adv. Chem. Ser. 175, American Chemical Society, Washington, D.C., 1979.
11. **West, R. N.,** *Adv. Phys.*, 22, 263, 1973.
12. **Green, J. H. and Lee, J.,** *Positronium Chemistry*, Academic Press, New York, 1964.
13. **Hautojarvi, P.,** *Positrons in Solids*, Springer-Verlag, West Berlin, 1979.
14. **Fluss, M. J., Gupta, R. P., Smedskjaer, L. C., and Siegel, R. W.,** *Positronium and Muonium Chemistry*, Ache, H. J., Ed., Adv. Chem. Ser. 175, Am. Chem. Soc., Washington, D.C., 1979, 243.
15. **Ache, H. J.,** *Positronium and Muonium Chemistry*, Adv. Chem. Ser. 175, American Chemical Society, Washington, D.C., 1979, 1.
16. **Madia, W. J., Nichols, A. L., and Ache, H. J.,** *Am. Chem. Soc.*, 97(18), 5041, 1975.
17. **Kirkegaad, P. and Eldrup, M.,** *Comput. Phys. Commun.*, 7, 401, 1974.
18. **Karchaudhari, S. N., Chang, F. C., Cheng, K. L., and Young, V. Y.,** *Anal. Chem.*, 53, 2048, 1981.
19. **Chang, C. C.,** *Characterization of Solid Surfaces*, Eds. Kane, P. F. and Larrabee, G. B., Plenum Press, New York, 1974, Chap. 20.
20. **Dlubek, G. and Brummer, O.,** *Ann. Phys.*, 43, 178, 1986.
21. **Venkateswaran, K.,** Positron Annihilation Spectroscopy for Chemical Analysis (PASCA), Dissertation, University of Missouri, Kansas City, 1985, 185.
22. **Pearson, R. M.,** *J. Catal.*, 23, 388, 1971.
23. **Osipow, L. I.,** Surface Chemistry, ACS Monograph No. 153, Reinhold Publishing Corp., New York, 1962, Chap. 3.
24. **Brunauer, S., Emmett, P. H., and Teller, E.,** *J. Am. Chem. SOC.*, 60, 309, 1938.
25. **Haneman, D.,** Characterization of Solid Surface, Kane, P. F. and Larrabee, G. B., Plenum Press, New York, 1974, Chap. 14.
26. **Sing, K. S. W.,** lecture on the significance of A. V. Kiselev's contribution to adsorption science, presented at the 60th Colloid and Surface Science Symposium, Atlanta, Georgia, June 15, 1986.
27. **Venkateswaran, K., Cheng, K. L., and Jean, Y. C.,** *J. Phys. Chem.*, 88, 2465, 1984.
28. **Leighly, H. P., Jr.,** *Appl. Phys.*, 12, 217, 1977.
29. **Venkateswaran, K., Jean, Y. C., and Cheng, K. L.,** unpublished results.
30. **Gauster, W. B.,** *J. Vac. Sci. Technol.*, 15, 688, 1978.
31. **Jain, P. C., Singru, R. M., and Gopinathan, K. P.,** Positron Annihilation, Proc. 7th Int. Conf., New Delhi, India, 1985.
32. **Zhou, X., Wang, S., Jaing, H., and Lung, C. W.,** Page 595.
33. **Venkateswaran, K., Cheng, K. L., and Jean, Y. V.,** *J. Phys. Chem.*, 89, 300, 1985.
34. **Venkateswaran, K.,** Positron Annihilation Spectroscopy for Chemical Analysis, Dissertation, University of Missouri, Kansas City, 1985, 157.
35. **Venkateswaran, K.,** Positron Annihilation Spectroscopy for Chemical Analysis, Dissertation, University of Missouri-Kansas City, 1985, 153.
36. **Talamoni, J., Abbe, J. Ch., Duplatre, G., and Haessler,** *Chem. Phys.*, 58, 13, 1981.
37. **Wikander, G.,** *Chem. Phys.*, 39, 309, 1979; **Wikander, G.,** *Chem. Phys. Lett.*, 77, 120, 1981.
38. **Solin, O.,** *Int. J. Appl. Radiat. Isot.*, 34, 1653, 1983.
39. **Goworek, T., Wawryszczuk, J., and Rybka, C.,** *Nukbeonika*, 21, 1157, 1976; **Weclawik, R., Wawryszczuk, J., Rybka, C., and Goworek, T.,** *Phys. Stat. Sol.*, b 95, K 113, 1979.
40. **Trane, N. and Evans, J. H.,** *Appl. Phys.*, 12, 183, 1977.
41. **Hsu, F. H., Robinson, M. O., and Hankla, R. H.,** *Phys. Lett. A*, 55A(1), 69, 1975.
42. **Venkateswaran, K., Cheng, K. L., and Jean, Y. C.,** *Positron Annihilation*, Jain, P. C., Singra, R. M., and Gopinathan, K. P., Eds., World Science Publishing Company, Singapore, 1985, 199; Venkateswaran, K., Positron Annihilation Spectroscopy for Chemical Analysis, Dissertation, University of Missouri, Kansas City, 1985, 193.
43. **Luo, X. H., Cheng, K. L., and Jean, Y. C.,** Positron Annihilation, Jain, P. C., Singru, R. M., and Gopinathan, K. P., Eds., World Science Publishing Co., Singapore, 1985, 971.
44. **Luo, X. H., Jean, Y. C., and Cheng, K. L.,** The Pittsburgh Conference and Exposition, Atlantic City, New Jersey, No. 510, March, 1987.
45. **Luo, X. H., Jean, Y. C., and Cheng, K. L.,** unpublished results.
46. **Sellschop, J. P. F., Madiba, C. C. P., Awnegarn, H. J., and Andeweg, A. H.,** *Nucl. Instrum. Methods Phys. Res.*, 218, 23, 1983.
47. **Washburn, E. W.,** *Proc. Natl. Acad. Sci.*, 7, 115, 1921.
48. **Riter, H. L. and Drake, L. C.,** *Ind. Eng. Chem. Anal. Ed.*, 17, 782, 1945.
49. **Drake, L. C.,** *Ind. Eng. Chem.*, 41, 780, 1949.
50. **Adamson, A. W.,** *Physical Chemistry of Surfaces*, 4th ed., John Wiley & Sons, 1982, 492.
51. **Perkal, M. B., and Walters, W. B.,** *J. Chem. Phys.*, 53, 190, 1970.
52. **Ito, Y., Yamashina, T., and Nagasaka, M.,** *Appl. Phys.*, 6, 323, 1975.
53. **Chuang, S. Y. and Tao, S. J.,** *J. Chem. Phys.*, 54, 4902, 1971.
54. **Hsu, F. H., Yang, M. M., and Wang, C. C.,** *Appl. Phys.*, 15, 85, 1978.
55. **Nakanish, H. and Ujihira, Y.,** *J. Phys. Chem.*, 86, 4446, 1982.
56. **Young, D. A.,** U.S. Patent 3,890,247, 1975.
57. **Luo, X. H., Cheng, K. L., and Jean, Y. C.,** Preliminary study of ammonium molybdate: the effect of calcination temperature, unpublished results, 1987.
58. **Jean, Y. C., Sandreczki, T. C., and Ames, D. P.,** *J. Poly. Sci.: Part B: Poly. Phys.*, 24, 1247, 1986.
59. **Ferrell, R. A.,** *Rev. Mod. Phys.*, 28, 308, 1956; Brandt, W., Berko, S., and Walker, W. W., *Phys. Rev.*, 120, 1289, 1960.
60. **Eldrup, M.,** Positron Annihilation, *Proc. Int. Conf. 6th*, Coleman, P. G., Sharma, S. C., and Diana, L. M., Eds., North-Holland, Amsterdam, 1982, 753.
61. **Brandt, W. and Spirn, I.,** *Phys. Rev.*, 142, 231, 1966.
62. **Fraissard, J.,** Catalysis by Zeolites, Imelic et al., Eds. 1980, 343.
63. **Millward, G. R., Thomas, J. M., Terasaki, O., and Watanabe, D.,** *Zeolites*, 6(2), 91, 1986.
64. **Media, W. J., Nichols, A. L., and Ache, H. J.,** Buncengesellschaft, *Phys. Chem.*, 78, 179, 1974.
65. **Media, W. J., Nichols, A. L., and Ache, H. J.,** *Appl. Phys.*, 3, 189, 1974.,
66. **Media, W. J., Nichols, A. L., and Ache, H. J.,** *J. Am. Chem. Soc.*, p. 5041, 1975.
67. **Luo, X. H., Cheng, K. L., and Jean, Y. C.,** Positron complex formation and its possible application in chemical and structural analysis, unpublished results.
68. **Luo, X. H., Cheng, K. L., and Jean, Y. C.,** Study in nitrates on alumina-supported catalysts, unpublished results.
69. **Luo, X. H., Cheng, K. L., and Jean, Y. C.,** Study of NO_2, SO_2 adsorbed on γ-alumina and Ni/γ alumina catalyst, unpublished results.
70. **Candia, R. et al.,** *Proc. Int. Congr. Catal.*, 8th ed., 2, 375, 1984.
71. **Candia, R. et al.,** Chemical Uses of Molybdenum, 4th Proc. Int. Conf., 1982, 374.
72. **Nielsen, B., Van Veen, A., and Lynn, K. C.,** Positron Annihilation, Jain, P. C., Singru, R. M., and Gopinathan, K. P., Eds., World Science

Publishing Co., Singapore, 1985, 836.

73. **Mills, A. P., Jr.,** Positron Solid State Physics, Brandt, W. and Dupasquire, A., Eds., North-Holland, 1983, 432.
74. **Lynn, K. G.,** Positron Solid State Physics, Brandt, W. and Dupasquire, A., eds., North-Holland, 1983, 609.
75. **Schneider, D. and Jean, Y. C.,** Positron Chemistry, North-Holland, in press.
76. **Venkateswaran, K., Luo, X. H., Cheng, K. L., and Jean, Y. C.,** 189th ACS National Meeting, Division of Fuel Chemistry Abstract, Miami Beach, FL, 1985, 266.
77. **Yang, S. X. R., Jean, Y. C., and Cheng, K. L.,** 21st ACS Midwest Regional Meeting, Phys. Chem. Div., Kansas City.
78. **Yang, S. X. R., Jean, Y. C., and Cheng, K. L.,** 190th ACS National Meeting, Coll. and Surf. Div., Chicago, 1985.
79. **Stump, R. and Talley, H. E.,** *Phys. Rev.*, 96, 904, 1954.
80. **Tripathy, D. N. and Bhuyan, M.,** Positron Annihilation, Jain, P. C., Singru, R. M., and Gopinathan, K. P., Eds., World Science Publishing Co., Singapore, 1985, 91.
81. **Hatano, T., Ohtake, K., Sato, E., Suzuki, A., Yamamoto, R., and Doyama, M.,** *Positron Annihilation,* Jain, P. C., Singra, R. M., and Gopinathan, K. P., Eds., World Science Publishing Co., Singapore, 1985, 599.
82. **Jean, Y. C., Nakanishi, H., Wang, S. J., Hardy, W. N., Hayden, M. E., Kiefl, R. F., Meng, R. L., Hor, H. P., Huang, J. Z., and Chu, C. W.,** *Phys. Rev.* B, 36, 3994, 1987.
83. **Dale, J. M., Hulett, L. D., Jr., Rosseel, T. M., and Fellers, J. F.,** 194th ACS National Meeting, Anal. Chem. Div., New Orleans, 1987.
84. **Nakanishi, H., Jean, Y. C., Smith, E. g., and Sandreczki, T. C.,** *J. Poly. Sci.* B, 27, 1419, 1989.