

THE EFFECT OF ALUMINIUM CITRATE ON ELECTROKINETIC POTENTIAL ON THE SURFACE OF QUARTZ AND TITANIUM DIOXIDE PARTICLES

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ABSTRACT

The electrophoretic mobility of quartz and titanium dioxide particles and the Al content and electrokinetic potential on their surface were measured. The effects of aluminium citrate (Al citrate) and AlCl_3 on them were also examined. The results show that both these particles are negatively charged, but the surface charge density of quartz is higher than titanium dioxide. Moreover, it was found that a certain amount of Al can be firmly bound on quartz surface under the pretreatment with Al citrate or AlCl_3 resulting in the decrease of their electrokinetic potential. In contrast, the significant changes of the Al content and electrokinetic potential on the surface of titanium dioxide particles pretreated by the same way could not be detected.

The present investigation provides further evidence for explaining the mechanisms of membrane damage caused by quartz and the antagonistic effect of Al citrate. Also, the probability of Al as a preventive measurement for silicosis in worksite was discussed in this paper.

INTRODUCTION

It has been demonstrated In Vitro that cytotoxic effect and membrane damage by quartz were much higher than by titanium dioxide under the same conditions of their dose and particle size. Al citrate can exert an antagonism against the toxicity of quartz by a possible mechanism of its action on the particle surface, but the effects of titanium dioxide on membranes were not affected by Al citrate, which may be attributed to the differences of both these particles in their surface structure and properties and the mechanisms involved in their interactions with cells.¹⁻⁴⁾

To evidence the hypothesis, the Al content, charge density and electrokinetic potential (—potential) on the surface of quartz and titanium dioxide particles were detected using the techniques of fluorescence and microelectrophoresis. The effects of Al citrate and AlCl_3 on them were also examined in the present study.

MATERIALS AND METHODS

Chemicals and Preparation

Quartz (99% pure) was supplied by Hygiene Institute of Chinese Prophylactic Medical Center. Particle diameter was all less than 5 μm , among which 89.3% was less than 2 μm and its specific surface was 4.59 m^2/g . The suspension was prepared at the concentration of 1 mg quartz/ml with deionized water. Al citrate with Al of 9.26% was supplied by Pharmaceutical Factory of Beijing Medical University and its solution was prepared at the concentration of 1 mg Al/ml with deionized water. The suspension of quartz plus Al citrate was prepared by Al citrate with 1 mg Al dissolved in 1 ml quartz suspension mentioned above. Quartz particles were

pretreated with a same Al amount contained in Al citrate or AlCl_3 solution. So called pretreatment, quartz or titanium dioxide particles were mixed proportionally with a certain Al amount contained in Al citrate or AlCl_3 solution. The suspension was centrifuged repeatedly, and washed with deionized water until Al in the last supernatant was not detected and then the precipitated particles were stored.¹ Titanium dioxide with a similar pure and size was obtained from Beijing Chemical Factory and its preparation was also as same as quartz. Fluorescence probe morin was purchased from Merck, Germany. The concentration of its stocked solution and applied solution were 500 $\mu\text{m}/\text{ml}$ ethanol and 50 $\mu\text{m}/\text{ml}$ ethanol, respectively.

Instrument and Conditions

Viscosimeter Model E (Japan), 25°C, shear transformation velocity 100 S-1.

Cell electrophoresis Autotimer Model Sx-2 (China), 25°C, voltage 40 V, electrode distance 5 cm, e.g. electric field intensity 8 v/cm.

Formulation (5): particle electrophoretic mobility (V)=L/E

L: mobility distance (μm) of particle in unit time (sec);

E: electric field intensity

The charged property of colloidal particle is expressed usually by its surface —potential as following:

$$\zeta = 6 \pi \eta L / DE.f(Kr) \quad (6)$$

D: dielectric constant of water, 78.54 at 25°C;
 η : medium viscosity (P);
 $f(Kr)$: coefficient related to size and shape of the determined particle, taken 1 usually in small spherical particle

Statistical Methods

F test

RESULTS AND DISCUSSION

The Determinations of Surface-Bound Al of Quartz and Titanium Dioxide Particles.

As shown in Figure 1 and 2, fluorescence excitation and emission peak position of Al citrate after the addition of morin shift all about 5 nm towards high frequency as compared to $AlCl_3$. However, Figure 3 and 4 illustrate that the difference disappears under the pretreatment of quartz particles with Al citrate or $AlCl_3$, and their excitation and emission are 440 nm and 515 nm, respectively, suggesting that ions such as Cl^- , citrate radical which may interfere with the determination have been washed out after the pretreatment and only Al remains to be bound on the surface of quartz particles. While fluorescence intensity of titanium dioxide pretreated with Al citrate is not only very low, but also its excitation and emission peak position exhibit blue shift about 15 nm and 10 nm, respectively. On the other hand, no Al can be detected on the surface of quartz or titanium dioxide particles without the pretreatment, indicating a little of their inherent Al. Policard et al has determined the surface-bound Al of quartz by X-diffraction.⁶ It is obvious that fluorescence label technique utilized in the present study is simple and sensitive and is used to do quantitative analysis.

The data listed in Table I show that: a) surface-bound Al of the pretreated quartz particles was increased with increasing Al dose to a certain extent, but not by proportion. It was also found that about 1:2 ratio of Al to quartz dose can prevent effectively the cytotoxicity or membrane damage from quartz in our other studies; b) the amount of surface-bound Al of quartz particles pretreated with a same Al dose is similar between Al citrate and $AlCl_3$; c) the pretreated quartz under the washing with HCl led their surface-bound Al not to be detected, then the antagonistic effect of Al disappeared and the toxicity of quartz recovered;⁽¹⁻²⁾ d) the amount of surface-bound Al of titanium dioxide pretreated with a same Al dose of Al citrate is still very low, which is consistent with the finding that its effect on cells or membranes was unable to be affected by Al citrate.²⁻⁴

The Determinations of Surface ζ -potential of Quartz and Titanium Dioxide Particles and the Effects of Al Citrate or $AlCl_3$

We began with the examination of medium viscosity due to its effect on electrophoretic mobility and surface ζ -potential of particles. From Table II, viscosity of Al citrate solution and the addition of quartz or titanium dioxide is higher, but medium viscosity was not influenced by the pretreatment with Al citrate or $AlCl_3$, suggesting that only free ions such as Al^{3+} presented in solution may affect medium viscosity.

It is seen from Table III, both quartz and titanium dioxide particles charge negatively but surface charge density of

quartz is much higher than titanium dioxide ($P < 0.01$), resulting in its higher electrophoretic mobility and surface ζ -potential, for instance, its ζ -potential value is 34.5% higher than titanium dioxide. Why quartz can interact with the choline groups charged positively in membranes leading

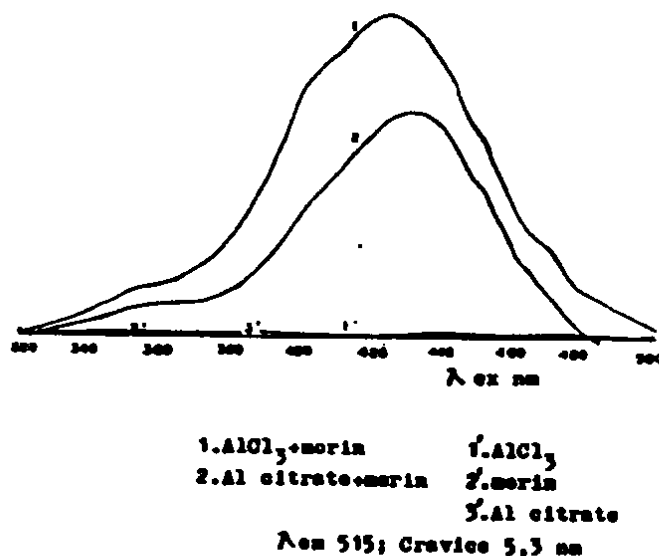


Figure 1. Fluorescence excitation spectra.

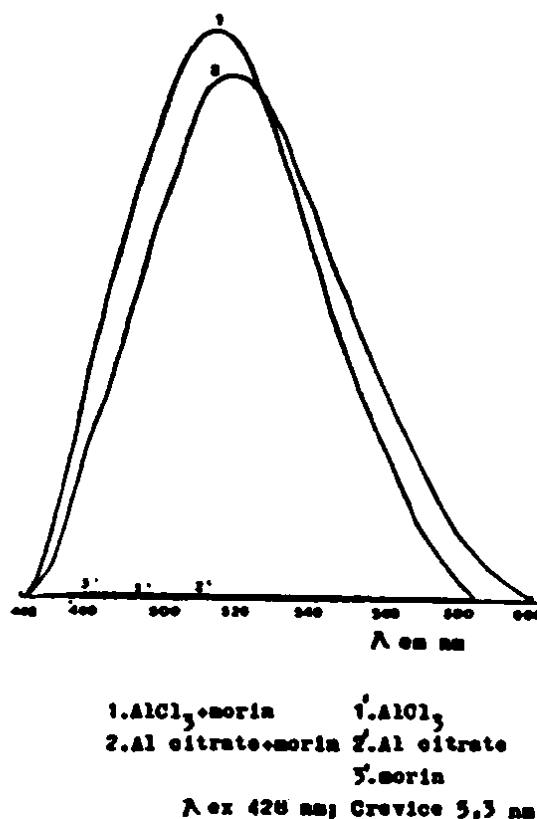
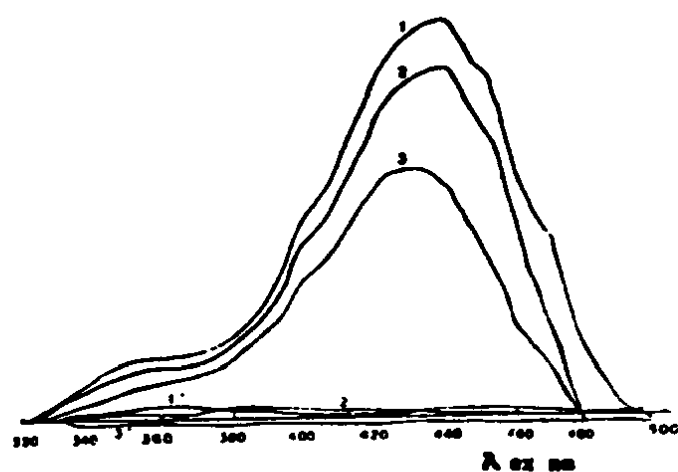


Figure 2. Fluorescence emission spectra.

Table I
Surface-bound Al of Quartz and Titanium Dioxide Particles Pretreated with Al Citrate or AlCl_3

Al dose	quartz		titanium	HCl washing
(μg)	$\mu\text{gAl/mg}$	nM Al/cm	$\mu\text{g Al/mg}$	
31.3	1.82	1.47	----	----
62.5	2.58	2.08	----	----
125.0	3.22	2.60	0.32	undetected
125.0*	2.99	2.41	----	undetected
250.0	3.12	2.52	----	----
500.0	3.16	2.55	----	----

The doses of quartz and titanium are all 300 μg . * AlCl_3

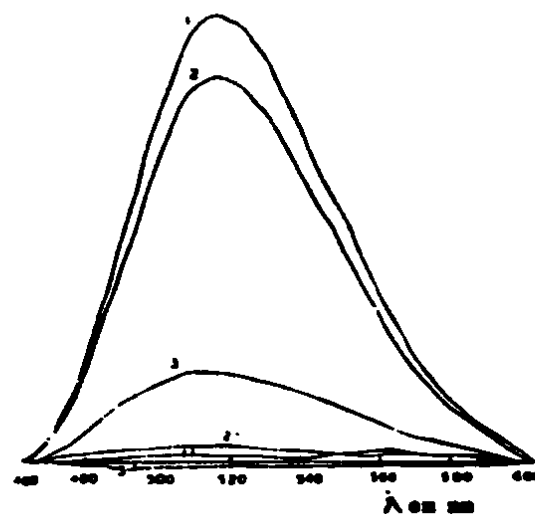


1. SiO_2 pretreated with AlCl_3 + morin
2. SiO_2 pretreated with Al citrate + morin
3. TiO_2 pretreated with Al citrate + morin
 $\lambda_{\text{em}} 515 \text{ nm}$; Crevise 5,3 nm

Figure 3. Fluorescence excitation spectra.

the increase of the negative charge density on the surface of macrophages may be just due to its larger inherent negative charge density and its higher affinity for $-\text{N}+(\text{CH}_3)_3$. As pointed out by Nolan, the more the negative charge is imparted by ionized silanol groups on quartz surface the stronger its haemolysis is.⁷

It is interesting to find the amount of surface-bound Al of quartz particles pretreated with Al citrate or AlCl_3 were not only increased significantly, but also their electrophoretic



1. SiO_2 pretreated with AlCl_3 + morin
2. SiO_2 pretreated with Al citrate + morin
3. TiO_2 pretreated with Al citrate + morin
 $\lambda_{\text{ex}} 428 \text{ nm}$; Crevise 5,3 nm

Figure 4. Fluorescence emission spectra.

mobility and surface ζ - potential were lowered markedly. Although the decrease of ζ - potential is less in the pretreatment than in quartz plus Al citrate without the washing, surface-bound Al of the pretreated particles is very firm, and plays an important role in pharmacology. The combination of quartz with Al by Si-O- Al bond can block the direct in

Table II
Medium Viscosity (η)

medium	η (cp)
Water	1.008
Solution of Al citrate	1.089
Suspension of quartz	0.996
Suspension of titanium dioxide	0.990
Suspension of quartz+Al citrate	1.071
Suspension of titanium dioxide+Al citrate	1.056
Suspension of quartz pretreated with Al citrate	1.002
Suspension of titanium dioxide pretreated with Al citrate	0.990

Table III
Electrophoretic Mobility (V) and Surface Electro Kinetic Potential (ζ -potential) of Quartz and Titanium Dioxide Particles and the Effects of Al Citrate on Them

Groups	V ($\mu\text{m}/\text{sec} / \text{v} / \text{cm}$)	ζ -potential (mv)	
	$\bar{X} \pm \text{SE}$	$\bar{X} \pm \text{SE}$	%
Quartz	4.051 \pm 0.075	87.5 \pm 1.6	100.0
Titanium dioxide	2.654 \pm 0.081	57.3 \pm 1.8	65.5
Quartz pretreated with AlCl_3	3.426 \pm 0.112	74.0 \pm 2.4	84.6
Quartz pretreated with Al citrate	3.381 \pm 0.118	73.1 \pm 2.5	83.5
Titanium dioxide pretreated with Al citrate	2.568 \pm 0.032	55.5 \pm 0.7	63.4
Quartz+Al citrate	2.296 \pm 0.062	54.0 \pm 1.5	61.7
	----	(49.6 \pm 1.4)	(56.7)
Titanium dioxide+Al citrate	2.173 \pm 0.048	51.4 \pm 1.1	58.7
	----	(46.9 \pm 1.1)	(53.8)

The values in brackets are theoretical values calculated except the effect of medium viscosity.

teraction of quartz with choline groups of membranes, so that the order structure and stability of membranes were maintained.

As compared with quartz, no significant decrease of surface ζ -potential of the particles was found after the addition of Al citrate to titanium dioxide suspension, a difference of ζ -potential occurred only between the theoretical value calculated except the effect of medium viscosity and the determined value of titanium dioxide itself ($P < 0.01$). However, there is no significant difference in ζ -potential between under the pretreatment with Al citrate and without the pretreatment ($P > 0.05$) (Table III). This fact indicates that surface-bound Al of titanium dioxide is very little and is

unable to change the structure and property of the particles and explains why its effect on cells or membranes can not be affected by Al citrate.

In deed, surface-bound cations like Al^{3+} of quartz will increase its nonpoisonous surface area resulting in the reduction of its toxicity, which will provide a clue for screening new drugs for silicosis. In addition, according to theory of electric double layer, whether collosol is stable in a certain condition will depend on the gravitational force and electrostatic repulsion among these particles. They will become easy to coacervate and sedimentate due to the reduction of their repellent potential energy and stability, if ζ -potential and charge of the colloidal particles are decreased. The

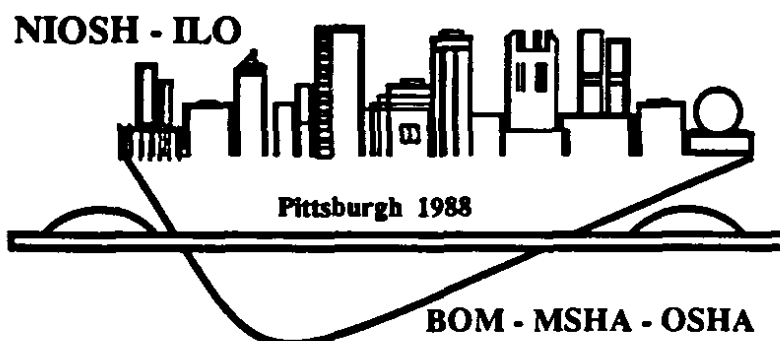
coacervation and sedimentation of these particles are not only beneficial in discharging from lung, but also in precipitation from the air. Therefore, it will be more efficient to prevent silicosis through the way changes the physical and chemical properties of the particles, so that their toxicity themselves will be lowered and their fall will be increased. It should be considered that a potential role of such cations as Al^{3+} plays in wet clearing dust, for example wet drilling.

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